

Chapter 4

Results and Discussion

4.1. Copolymerization of Indene:

Indene has been selected as a common monomer with different vinyl monomers because it has wide use in the field of technology. The incorporation of five member planar ring of the indene monomer into the backbone chain could lead to copolymers of great stiffness as well as a higher thermal stability. The data concerning the copolymerization are represented in table (4.1) and (4.2) respectively and are plotted in figure (4.1).

Table (4.1): Copolymerization data of In/AN copolymers.

Monomer Composition Mole %		% N	Copolymer Composition Mole %	
In	AN		In-co-AN	AN
10	90	19.5	13.21	86.79
20	80	15.55	23.50	76.50
30	70	12.79	32.07	67.93
40	60	10.66	39.63	60.37
50	50	8.9	46.70	53.25
60	40	8.13	50.10	49.90
70	30	5.75	61.65	38.35
80	20	4.13	70.76	29.24
90	10	2.29	82.58	17.42

Table (4.1): Copolymerization data of In/AA copolymers.

Monomer Composition Mole %		% C	Copolymer Composition Mole %	
In	AA		In	AA
10	90	53.90	5.83	94.17
20	80	58.85	10.52	89.48
30	70	60.81	17.24	82.76
40	60	63.91	22.86	77.14
50	50	66.86	28.57	71.43
60	40	69.71	34.41	65.59
70	30	72.61	40.69	59.31
80	20	75.73	48.02	51.98
90	10	80.06	59.10	40.99

where N % and C % are the percent of the nitrogen and carbon contents respectively in the copolymes.

The data in tables (4.1) and (4.2) were analyzed according to the methods of Fineman-Ross ⁽⁵⁰⁾ and Kelen- Tüdös ⁽⁵²⁾ and were investigated in tables (4.3) and (4.4) respectively.

Table (4.3): Analysis of the copolymerization data of In & AN in DMF at 60 °C by F-R and K-T methods.

F	G	ξ	η
		$\alpha=1.176$	
0.081	-0.619	0.065	-0.495
0.203	-0.564	0.148	-0.411
0.389	-0.479	0.25	-0.307
0.677	-0.349	0.366	-0.189
1.139	-0.139	0.493	-0.06
2.241	0.006	0.657	0.002
3.387	0.882	0.743	0.194
6.612	2.347	0.85	0.302
17.089	7.101	0.936	0.389

Table (4.4): Analysis of the copolymerization data of In & AA in DMF at 60 °C by F-R and K-T methods.

F	G	ξ	η
		$\alpha=3.346$	
0.199	-1.683	0.056	-0.474
0.532	-1.877	0.137	-0.484
0.882	-1.629	0.208	-0.385
1.499	-1.582	0.309	-0.326
2.5	-1.5	0.427	-0.256
4.289	-1.359	0.561	-0.1778
7.934	-1.067	0.703	-0.095
17.316	-0.329	0.838	-0.016
56.272	2.747	0.944	0.046

$F=X^2/Y$, $G=X(Y-1)/Y$, $\xi=F/(\alpha+F)$, $\eta=G/(\alpha+F)$, α is an arbitrary constant

The data from these tables were plotted; one set represents the Finman-Ross as shown in figure (4.2), the other one illustrates the Kelen-Tüdös in figure (4.3).

The reactivity ratios r_1 of indene and r_2 of the other monomers were calculated as the slopes and intercept the lines. The data are summarized in Table 5.

Table (4.5): Apparent reactivity ratios values for In (M_1) and AN and AA (M_2).

	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
	F-R method			K-T method		
AN	0.46	0.70	0.32	0.99	0.66	0.65
AA	0.08	1.73	0.14	0.06	1.76	0.11

The calculated reactivity ratios r_1 and r_2 were used to build theoretical composition curves and were adjusted to fit the experimental data. The calculated curve is shown in figure (4.3) together with the experimental points.

The product of r_1r_2 serves as a measure for the tendency of the alternation of the two monomers in the polymer chain. Perfect alternation is achieved where $r_1r_2 = 0$. The high tendency for alternation is in the binary system of In/AN copolymers.

Figure (4.2) and (4.3) illustrates the tendency of alternation, since the resulting copolymer composition is close of 50% of the monomers for a big range of monomer compositions.

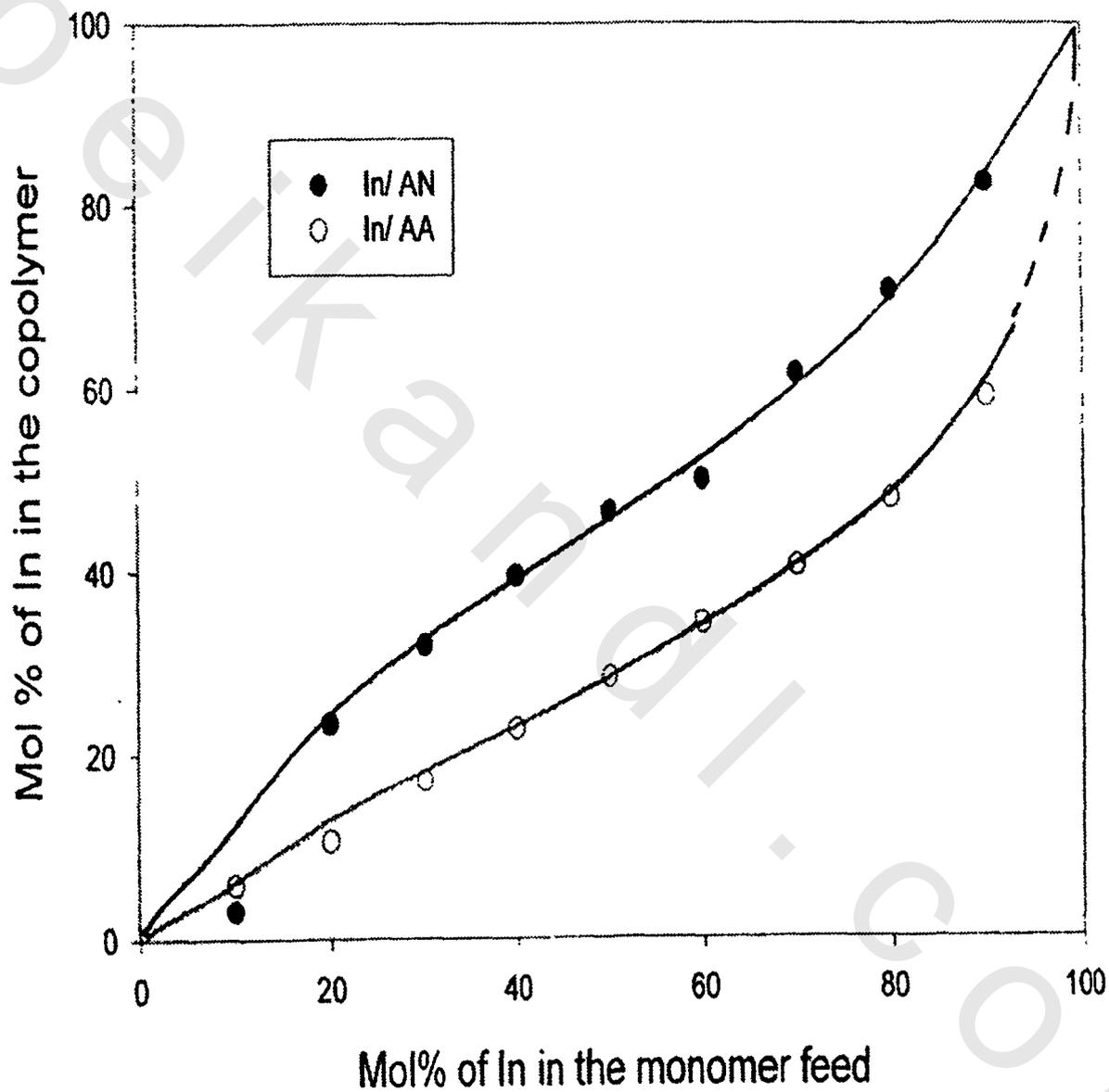


Figure (4.1): Copolymerization of In (M_1) with AN and AA (M_2) in DMF at 60 °C.

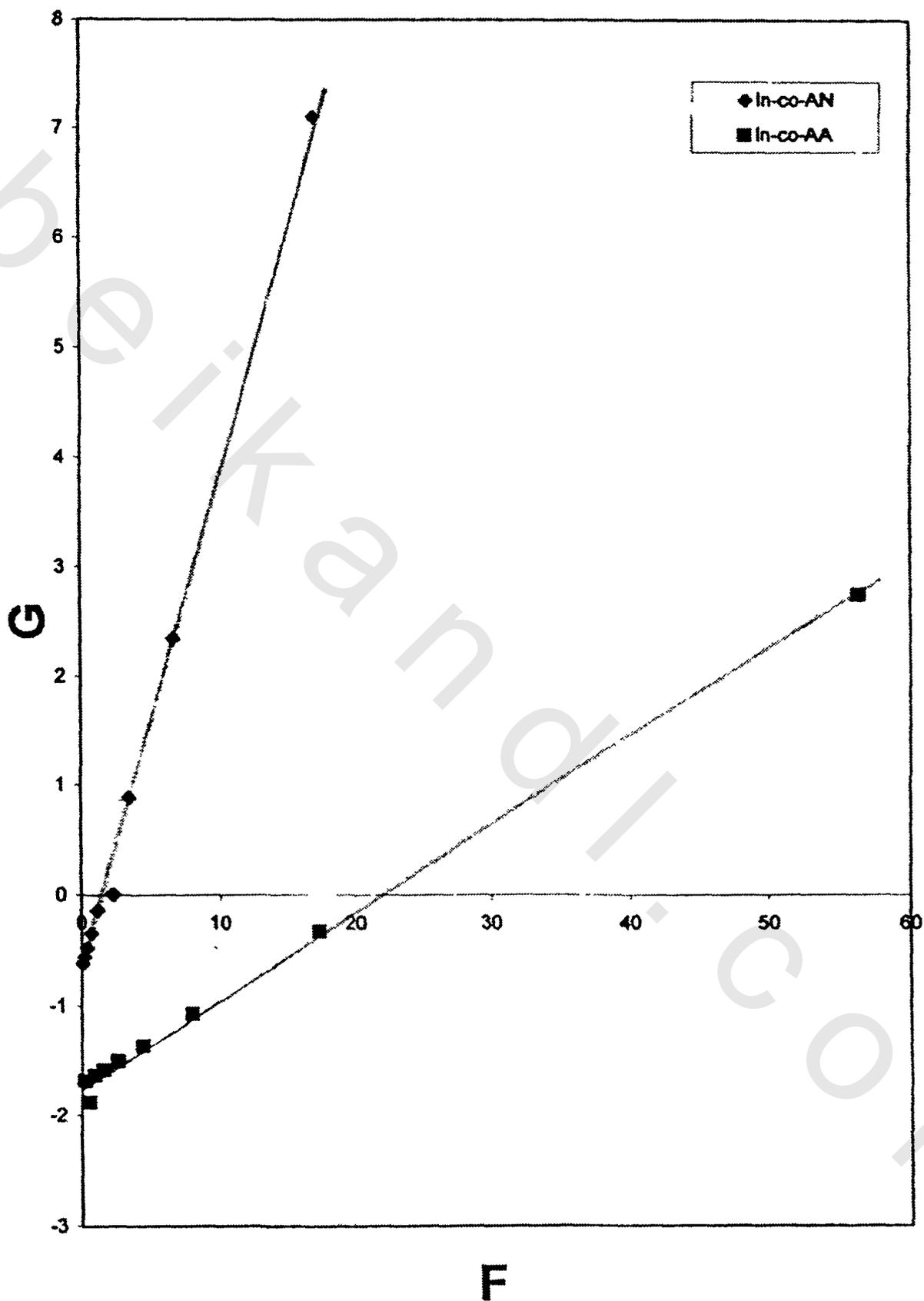


Figure (4.2): Finman-Ross plots for In (M_1) and AN and AA (M_2) in DMF at 60 °C

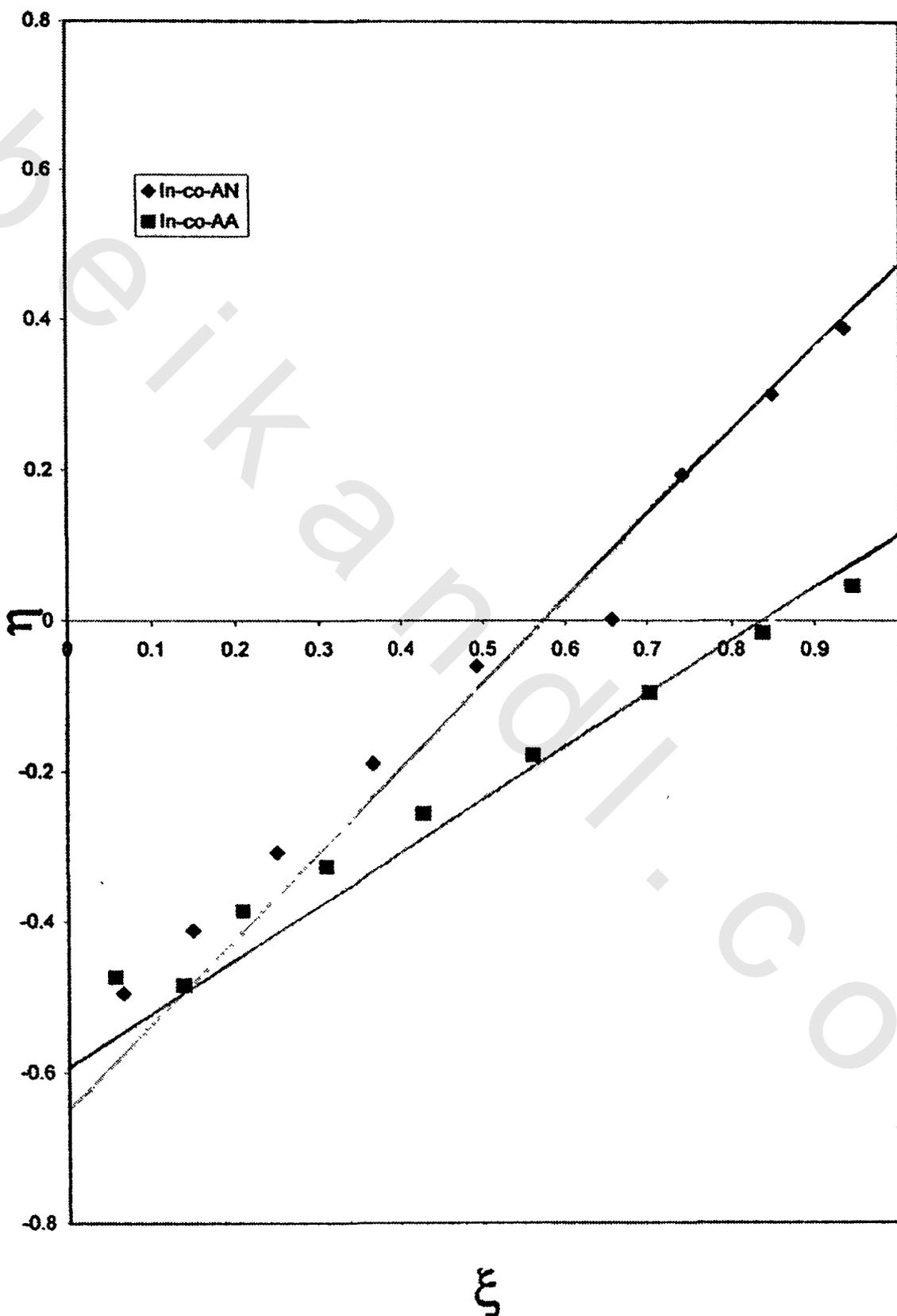


Figure (4.3): Kelen-Tüdös plots for In (M_1) and AN and AA (M_2) in DMF at 60 °C.

4.2. The Spectral Analysis:

4.2.1. The FTIR Spectrum of the Polymers:

The FTIR spectra of the investigated homopolymers poly In, poly AN and poly AA as well as the copolymers of the binary system of In/AN and In/AA of different compositions are shown in figures (4.4) to (4.8).

The absence of the absorption band at 1640 cm^{-1} characteristic of the carbon-carbon double bond, in all the investigated systems clearly indicates that a true homopolymer and a copolymer are formed in all cases.

The spectra in the figures indicate the appearance of the bands at $2875\text{-}3080\text{ cm}^{-1}$ region which can be assigned to the aromatic and aliphatic C-H stretching modes. Also, the appearance of the band in $744\text{-}750\text{ cm}^{-1}$ of the substitution five adjacent hydrogen atoms and the absorption band in 1724 cm^{-1} and 1631 cm^{-1} of the carbonyl group (C=O).

The bands in 2235 cm^{-1} and 1660 cm^{-1} for the CN⁽⁵³⁾ and CN stretching and bands in 1708 and 1652 cm^{-1} for the carbonyl groups of the carboxylic acid. Therefore all the observational bands are evidence for confirming the formation of indene copolymers with acrylic acid and acrylonitrile respectively.

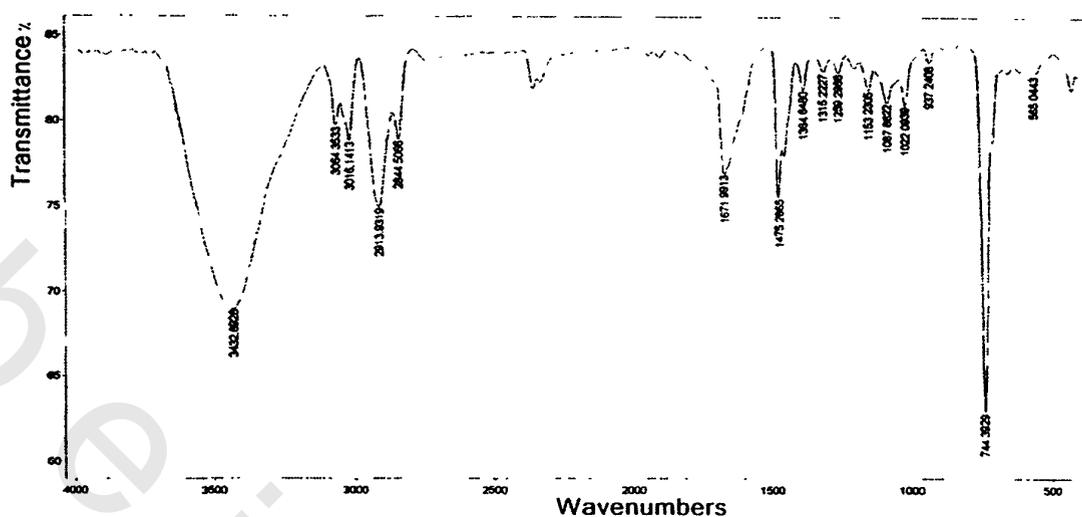


Figure (4.4): FTIR Spectrum of Polyindene.

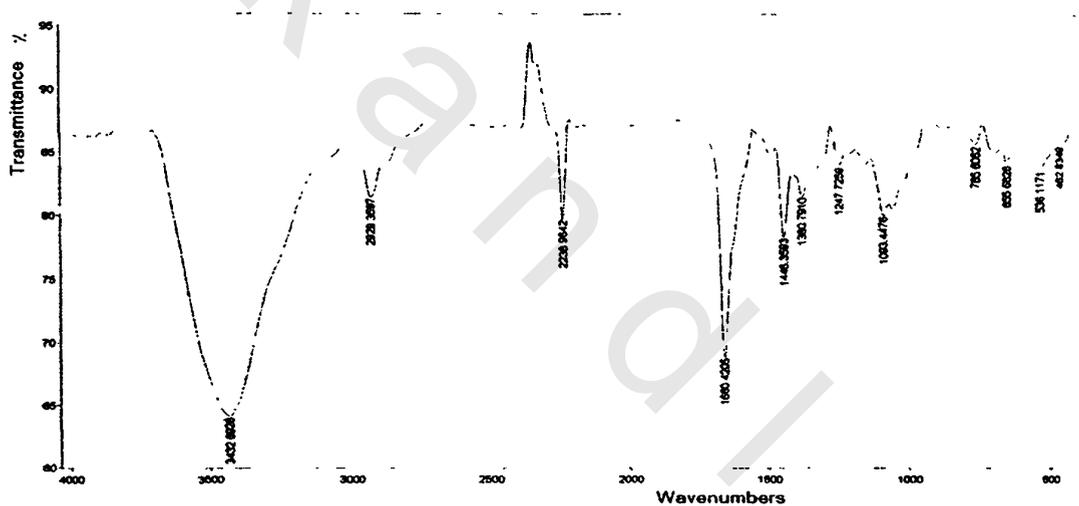


Figure (4.5): FTIR Spectrum of PAN.

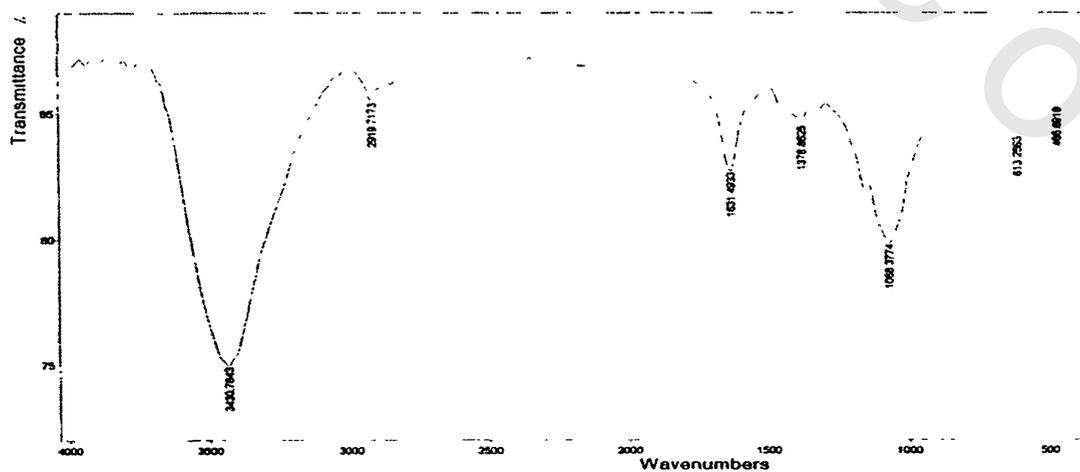


Figure (4.6): FTIR Spectrum of PAA.

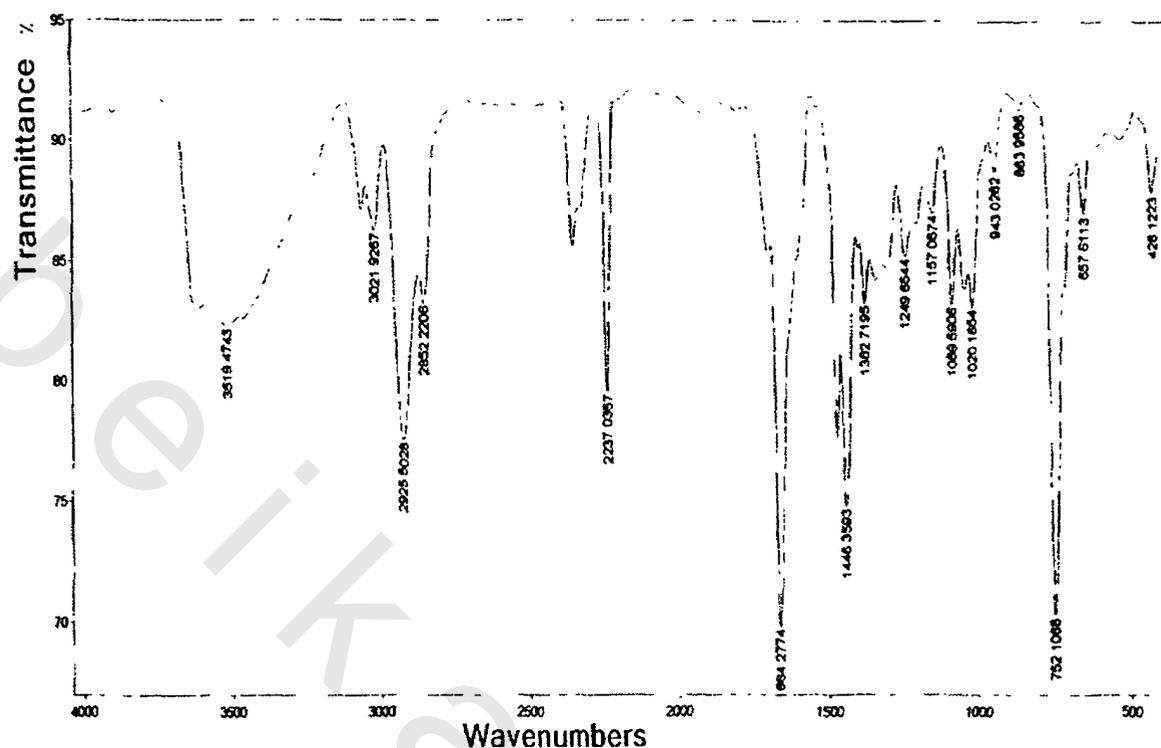


Figure (4.7): FTIR Spectrum of sample 20/80 In/AN.

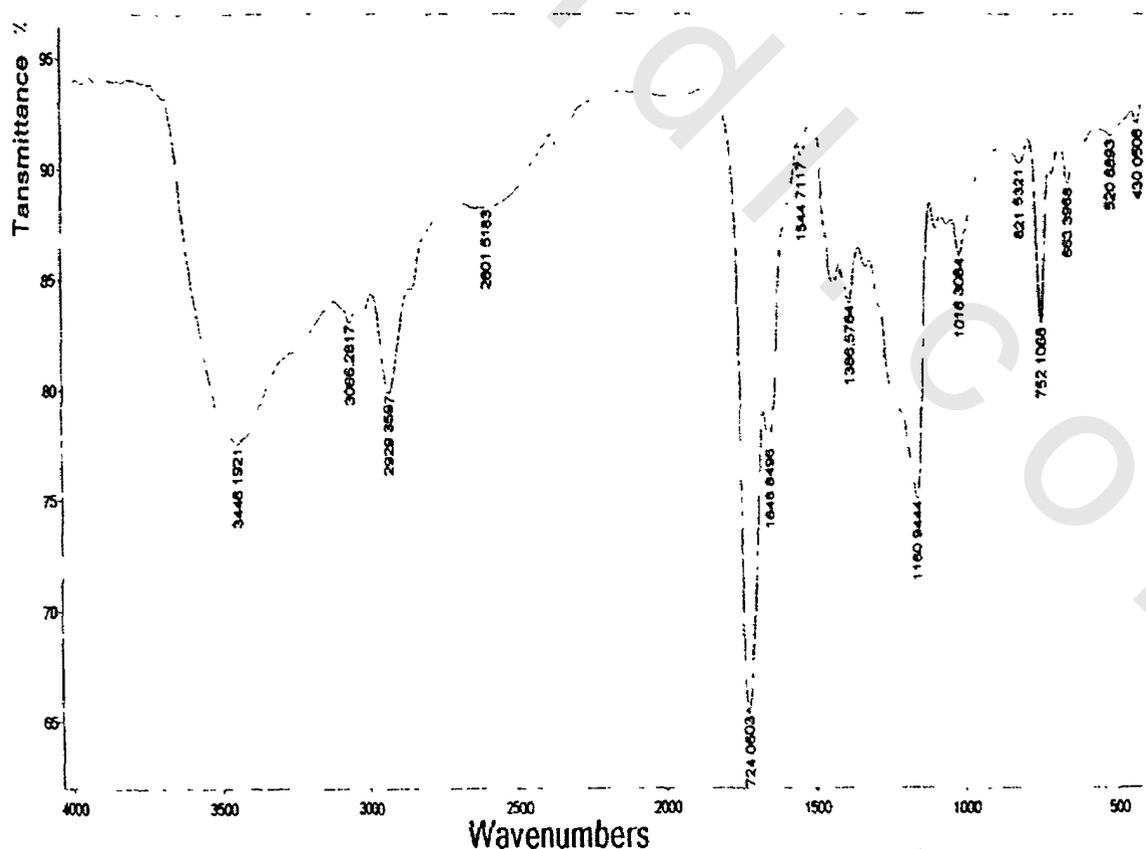


Figure (4.8): FTIR Spectrum of sample 50/50 In/AA.

4.3. X ray Diffraction:

Unlike simple inorganic compounds, polymers don't have a perfectly ordered crystal lattice. In fact, they contain both crystalline and amorphous regions ⁽⁵⁴⁾. The crystalline and amorphous components influence polymer properties. The degree of crystallinity is, of course, based on the premise that crystalline and non-crystalline components of a polymer can coexist. The degree of crystallinity is a great technological and practical importance and several methods which don't always produce precisely the same results have been devised to measure it. The degree of crystallinity can be calculated by knowledge of the densities of the crystalline and amorphous components of a polymer or by measure the specific volume of the polymer ⁽⁵⁵⁾ sample. Nevertheless, an approximate of the crystallinity can be obtained from the simple construction of a horizontal baseline is drawn between the extremities of scattering curve Figure (4.9 a, b) to remove the background scattering and the area under the peaks were determined. The degree of crystallinity is given by the following equation:

$$\chi = A_c / (A_c + A_{am}) * 100$$

where A_{am} is the area under the amorphous hump and A_c is the area remaining under the crystalline peak. Table (4.6) indicates the χ of crystallinity of the prepared copolymer.

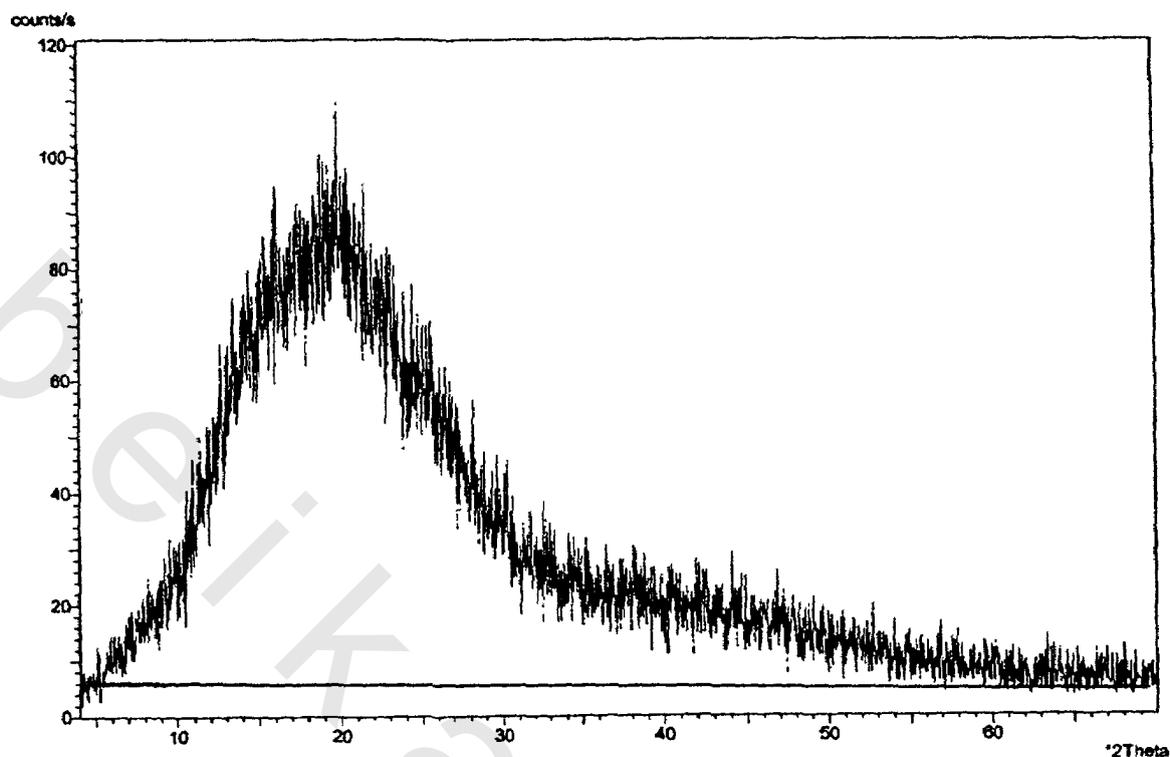


Figure (4.9 a): The X-ray diffraction pattern of the copolymer of In/AN of 50/50 molar ratio.

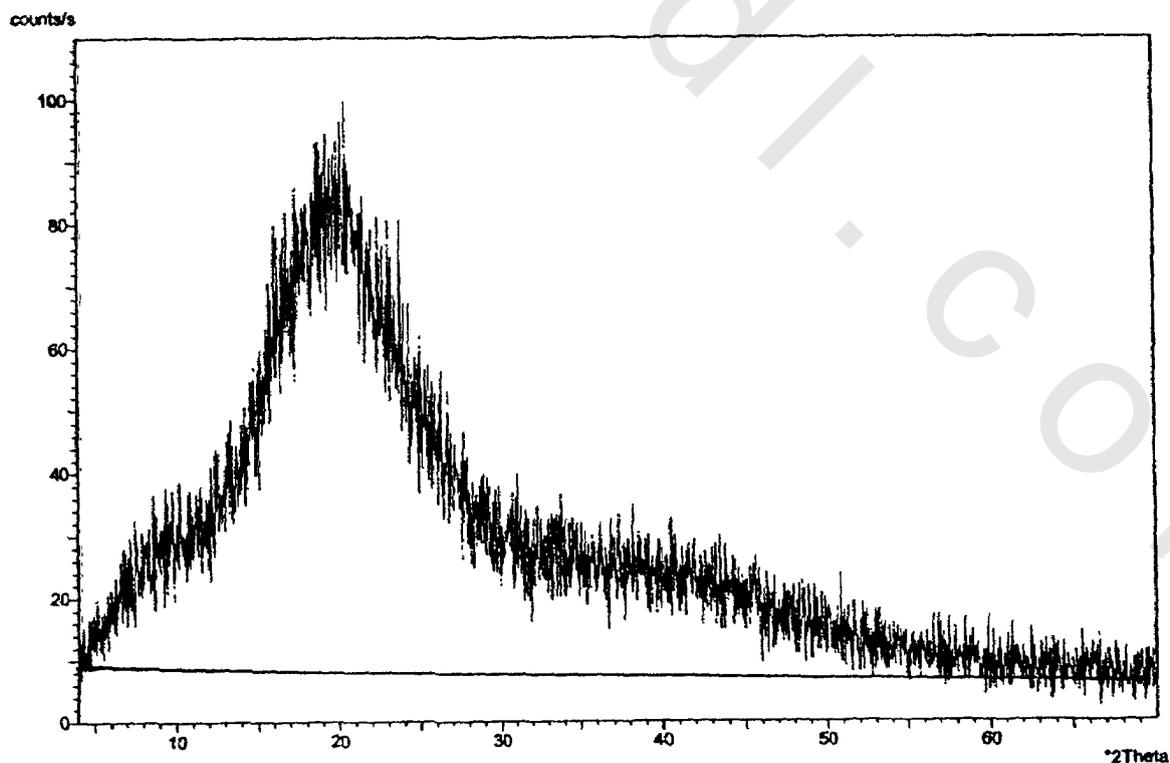


Figure (4.9 b): The X-ray diffraction pattern of the copolymer of In/AA of 50/50 molar ratio.

Table (4.6): The values of the ratio of crystallinity and amorphous in the copolymers.

The copolymer	% Crystal	% Amorphous
In/AN (50/50)	48.77	51.19
In/AA (50/50)	47.41	52.62

The data in table (4.6) shows that the crystal and non-crystal components of the In/AN and In/AA copolymers are the same.

4.3. Thermal Analysis:

4.3.1. Thermogravimetric Analysis (TGA):

Thermal analysis is a powerful tool frequently used to characterize and evaluate the thermal stability of polymeric materials. Thermal resistance is defined as the temperature of incipient thermal as thermo-oxidative degradation of the polymer accompanied by the elevation of the volatile products. As a result, the weight of the polymer specimen decreases, the determination of this loss in weight is the principle of different variants of Thermogravimetric analysis TGA ⁽⁵⁵⁾. The temperature at which the loss in weight occurs is considered to be the thermal stability of resistance of the polymer.

The obtained results reveal that polyindene has a relatively high thermal stability in addition to improve the thermal properties of the prepared polymer; indene was used together with acrylonitrile or acrylic acid.

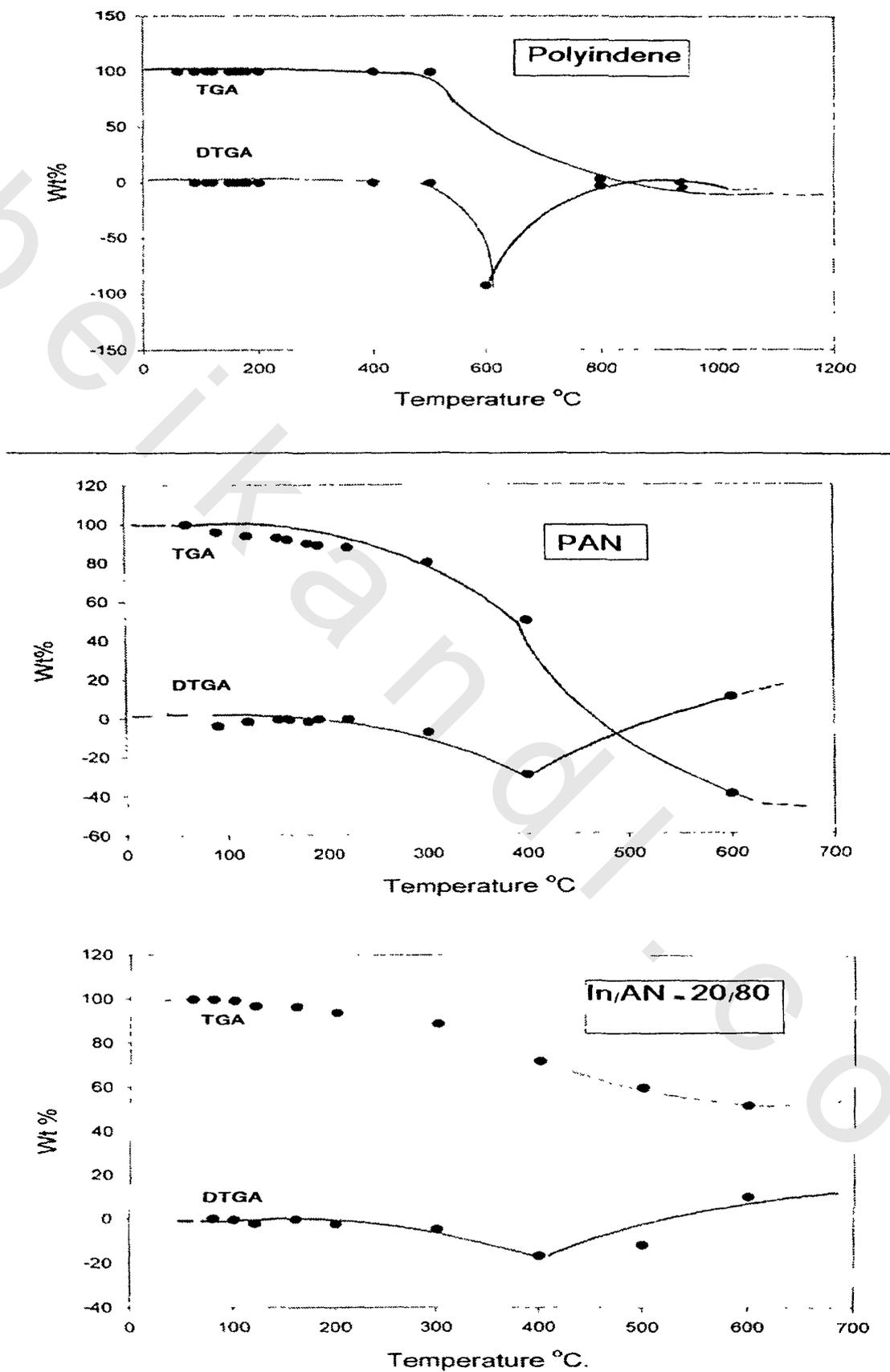


Figure (4.10): The TGA and DTGA thermogram of polyindene, Polyacrylonitrile and their copolymer.

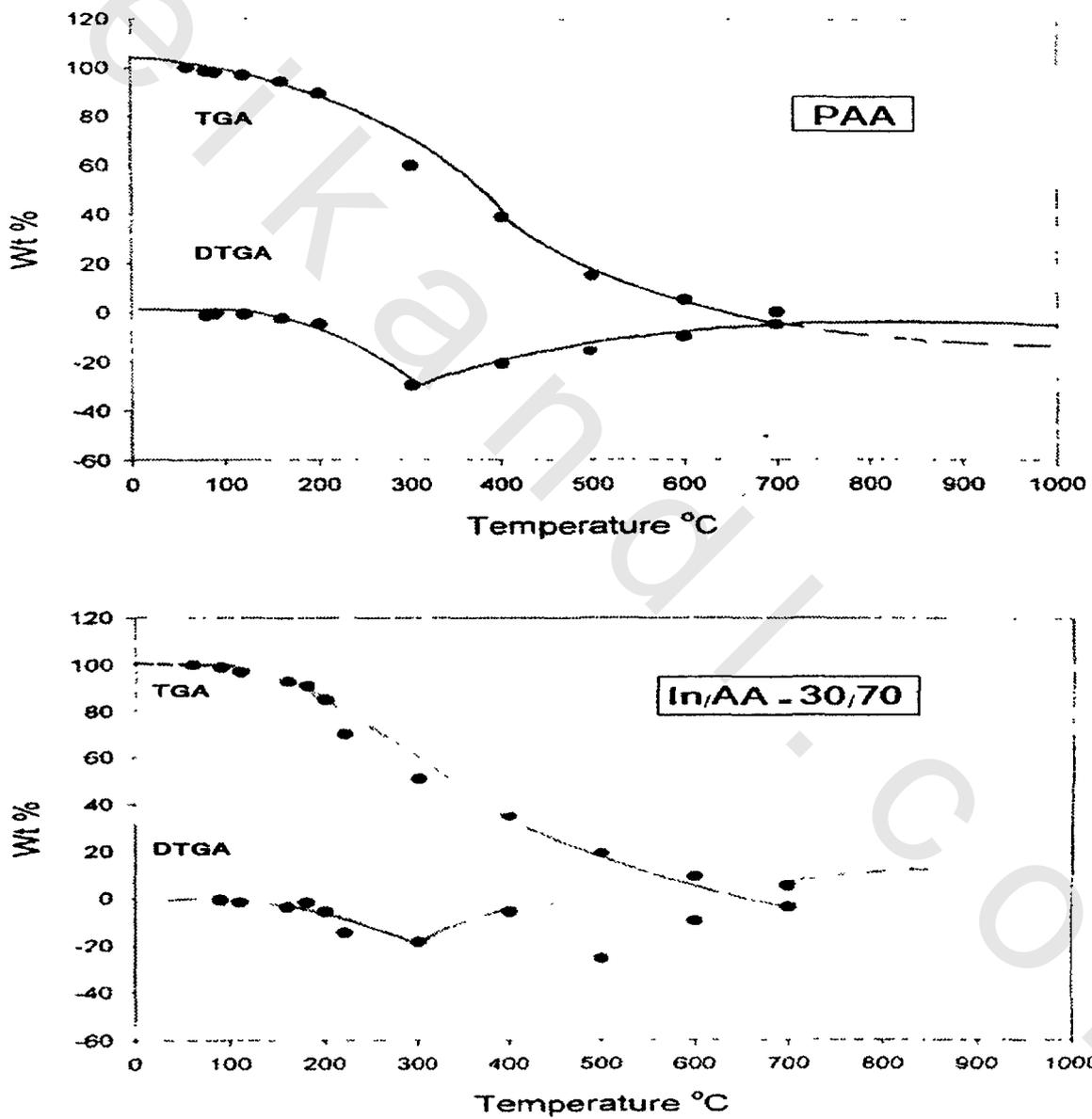


Figure (4.11): The TGA and DTGA thermogram of Polyacrylic acid and In/AA copolymer.

The TGA and DTGA curve of polyindene, polyacrylonitrile and their copolymer are given in figure (4.10), while the TGA and DTGA of polyindene and polyacrylic acid and their copolymer are given in figure (4.11), respectively. Polyindene shows a thermogram with an initial decomposition temperature (IDT) at 480 °C and the final decomposition temperature or the maximum decomposition occurred at 600 °C. The initial decomposition of polyacrylonitrile and the copolymer of In/AN of 30/70 mol % are 280 and 300 °C respectively, and the maximum decomposition temperature at 400 and 500 °C respectively. The initial decomposition temperatures of polyacrylic acid and the copolymer of In/AA of 30/70 molar ratio are 250 and 270 °C respectively, while the maximum decomposition at 300 and 300 °C respectively. Polyindene showed a good thermal stability and improve the thermal stability of AN and AA also, the system of In /AN give more thermal stable material than In/AA because PAA is easy to decaroxylate by loosing COOH group.

4.3.2. Differential Scanning Calorimetry (DSC):

Figures (4.12), (4.13) and (4.14) show the DSC thermogram of the homopolymers, and the copolymers of In/AN and In/AA respectively. The thermogram starts from the room temperature up to 400 °C. The glass transition temperatures of all the samples are detected as a small peak which appears in the thermogram of each sample because the heating rate was 5°/min. The glass transition temperatures of the samples were determined from the DSC thermogram and listed in Table (4.7).

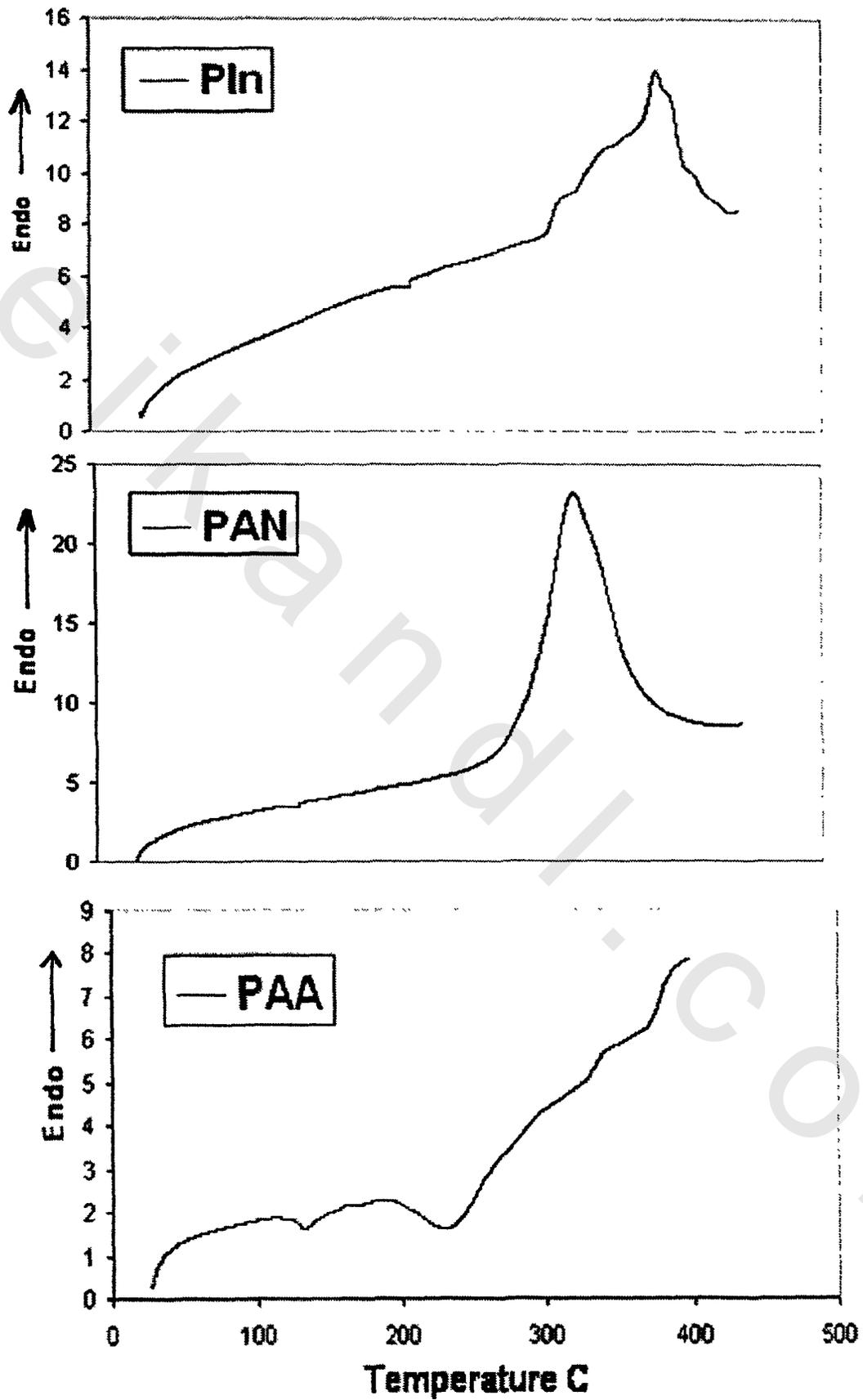


Figure (4.12): DSC thermogram of the homopolymers.

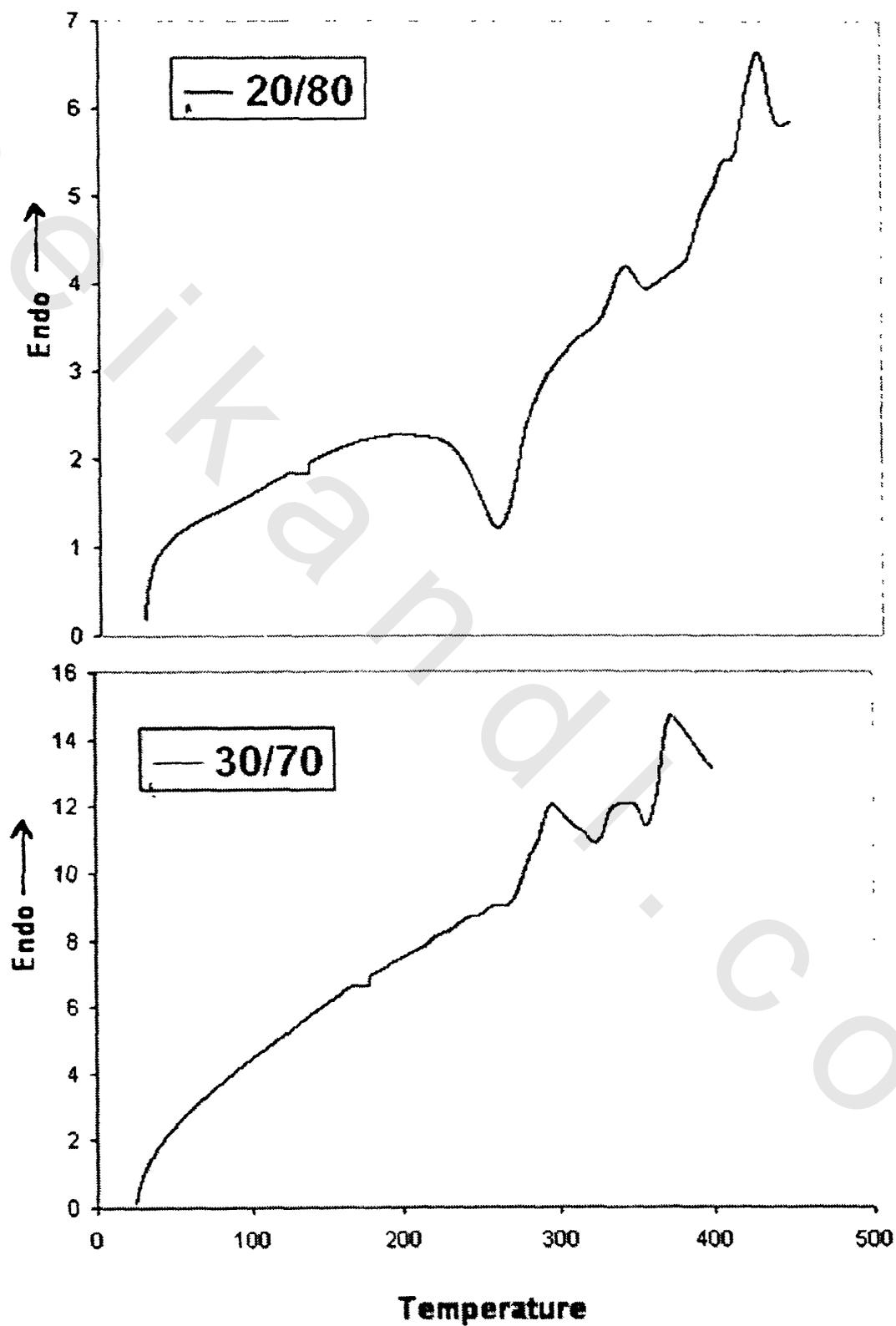


Figure (4.13): DSC thermogram of the In/AN Copolymers.

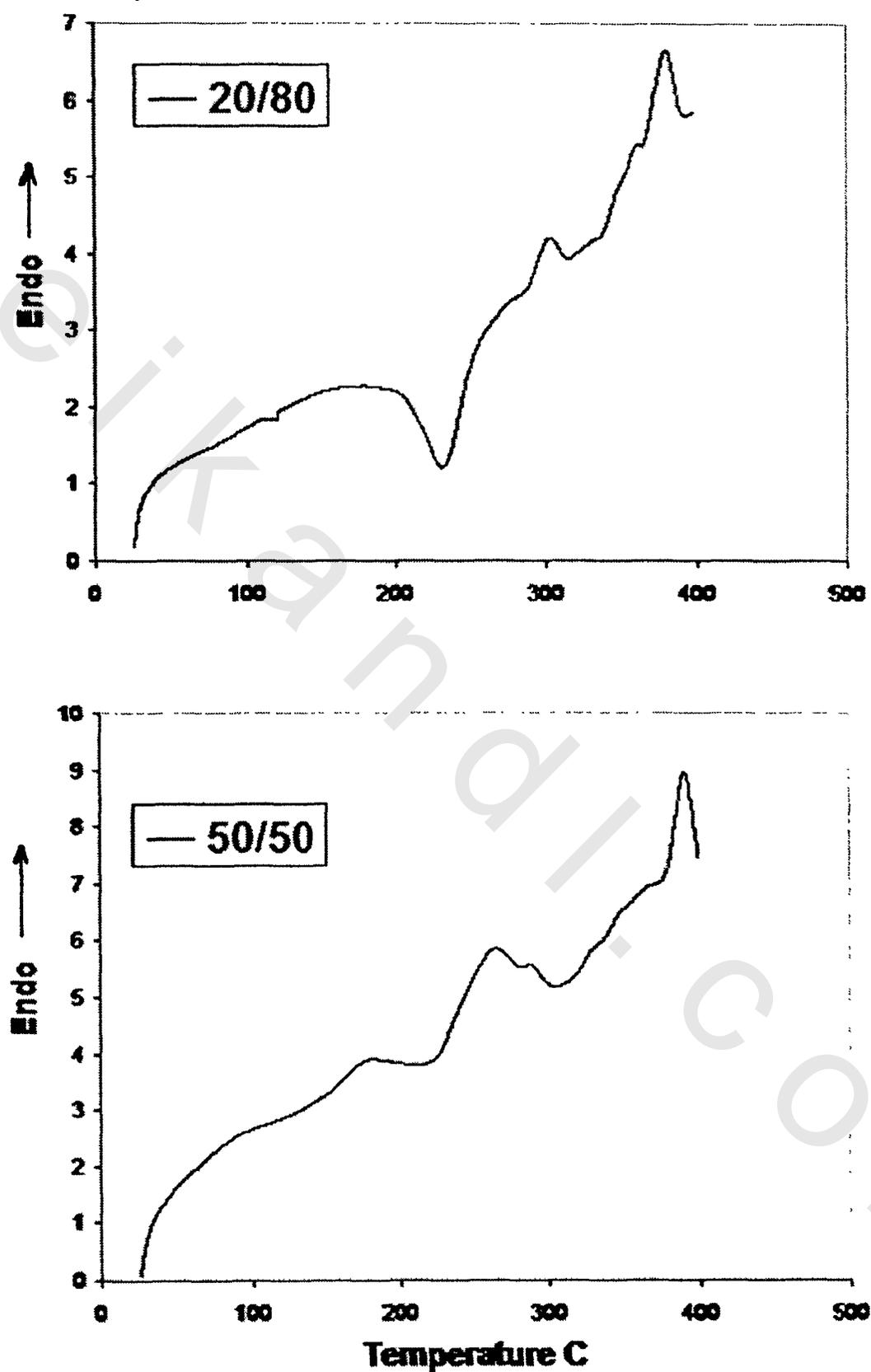


Figure (4.14): DSC thermogram of the In/AA Copolymers.

Table (4.7): The values of the glass transition temperatures of the investigated sample.

polymer	PIn	PAN	PAA	20/80 In/AN	30/70 In/AN	20/80 In/AA	50/50 In/AA
T _g °C	196	133	125	150	177	120	132

It is shown from the table that polyindene possesses the highest glass transition temperature. This is because of its cyclic structure; phenyl rings of Polyindene are arranged horizontally along the main chain; hence the repeating unit of Polyindene forms a nearly planar structure. This unique structure renders polyindene having high glass transition temperature⁽⁵⁶⁾. Thus the T_g of the different copolymer increases as the mol% of the indene in the copolymer increases as it is shown from the above table.

Thermal conductivity can be determined from the thermogram at each peak for each sample. The thermal conductivity was calculated from Spiel relation⁽⁴⁷⁾ who states that the peak area is proportional to the reciprocal of the thermal conductivity k when g , m and ΔH are constants.

$$\text{Area} = m (\Delta H) / g k$$

Where g is the geometrical shape constant of the apparatus, m is the mass of the sample and ΔH is the difference in the heat content of 1 gm of the specimen before and after the reaction. The values of the calculated thermal conductivity and the temperature of each peak were listed in Tables (4.8), (4.9) and (4.10).

It is clear from the table that the thermal conductivity k of the homopolymers increases with increasing the temperature after melting in the liquid state. This may be due to increasing the phonon velocity under the effect of the thermal energy, also may be due to the softening of the samples which occurs gradually with increasing the temperature. This softening is associated with increasing the mobility of the charge carriers, as well as increasing the thermal conductivity.

Table (4.8): The Values of the thermal conductivity of the homopolymers.

Polymer	Temperature °C	Thermal Conductivity W/m K
PIn	289.57	$1.06 \cdot 10^{-7}$
	299.04	$1.28 \cdot 10^{-7}$
	348.49	$2.22 \cdot 10^{-7}$
PAN	296.8	$3.81 \cdot 10^{-10}$
PAA	132.06	$2.42 \cdot 10^{-7}$
	229.21	$4.05 \cdot 10^{-7}$
	321.7	$5.18 \cdot 10^{-7}$
	366.84	$6.31 \cdot 10^{-7}$

In addition, it has been indicated that PAA possesses relatively higher values of " k " than that of PIn and PAN as shown in Table (4.7). The higher values of the thermal conductivity of PAA may be attributed to the high polarity of the carboxylic groups possessed to PAA which are rotating under the effect of the thermal energy.

Table (4.9) investigates the temperature dependence of the thermal conductivity for In/AN copolymers. It is clear from the table that, the sample with 20/80 In/AN mol% has higher k values than that

of sample 30/70 In/AN mol%. Similarly Table (4.10) shows the temperature dependence of the In/AA copolymers with two different molar ratios of In/AA 20/80 and 50/50. It is shown from the Table that the sample of 20/80 mol% possesses higher values of k than that of sample with 50/50 mol%. This behavior explains that the thermal conductivity of the copolymers decreases with increasing the mol% of the indene in the copolymer.

Table (4.9): The Values of the thermal conductivity of the In/AN copolymers at different molar ratios.

Polymer	Temperature °C	Thermal Conductivity W/m K
In/AN 20/80	240.65	$1.52 \cdot 10^{-6}$
	277.60	$1.79 \cdot 10^{-6}$
	315.81	$1.93 \cdot 10^{-6}$
In/AN 30/70	268.74	$7.68 \cdot 10^{-8}$
	322.67	$1.23 \cdot 10^{-7}$
	371.41	$2.40 \cdot 10^{-7}$

Table (4.10): The Values of the thermal conductivity of In/AA copolymers at different molar ratios.

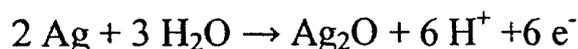
Polymer	Temperature °C	Thermal Conductivity W/m K
In/AA 20/80	230.80	$4.45 \cdot 10^{-8}$
	304.15	$5.65 \cdot 10^{-7}$
	380.77	$9.11 \cdot 10^{-7}$
In/AA 50/50	134.11	$1.17 \cdot 10^{-7}$
	221.53	$2.19 \cdot 10^{-7}$
	279.32	$2.56 \cdot 10^{-7}$
	305.51	$3.04 \cdot 10^{-7}$
	390.15	$4.90 \cdot 10^{-7}$

4.4. Electrical Conductivity:

The polymer conductivity depends upon the presence of free ions not connected chemically with the polymer chains, while the chain proper doesn't participate in the charge transfer process. Thus, polymer conductivity depends greatly on the presence of low molecular weight impurities which can serve as the ion source. There are two possible ion sources:

- (i) The dipole orientation by thermal agitation.
- (ii) Ions injected from metal electrode into the polymer.

These injected ions may be generated as a result of the reaction between the electrode and the ambient atmosphere to form metal oxide layer according to the relation ⁽⁵⁷⁾:



4.4.1. AC Conductivity of the Homopolymers:

- σ_{ac} of Polyindene PIn:

Figure (4.15) is a set of typical curves correlating $\ln \sigma$ and the reciprocal of absolute temperature for PIn, at different frequencies ranging from 100 KHz to 1 MHz. It is clearly shown from the figure the presence of phase transition and/ or a change in the electrical conduction around the temperatures $T = 338 \text{ K}$ and $T = 363 \text{ K}$. To

check what the correct possibility is, it is of interest to combine here the data of the thermal parameters, mainly the TGA and DSC thermograms. As one can see from figure (4.4) the TGA thermogram of polyindene failed to show any loss in weight, furthermore figure (4.12) the DSC thermogram of PIn indicates the absence of any phase change at that temperatures. Thus the change in the electrical conductivity at that temperature is therefore most probably due to change in the conduction mechanism rather than phase change.

In other words, one may propose two types of conduction existing in Polyindene, one at low temperature (below 338 K) and the other at high temperature (above 363 K) by the regime of extrinsic and intrinsic conduction respectively ⁽⁵⁸⁾. This possibility has been confirmed and supported from Arrhenius relation which describes regions I and III:

$$\sigma_T = n_o \mu_e e^{-E_a / KT} \quad (4.1)$$

where n_o is the number of the charge carriers per unit volume, e is the electronic charge, μ_e is the mobility charge carriers, E_a is the activation energy of the process, K is the Boltzman's constant and T is the absolute temperature. Usually the extrinsic conduction is due to ion vacancies and /or defects. On the other hand, in the intrinsic range the conductivity is predominantly due to the movement and tunneling of vacancies produced by the thermal activation ⁽⁵⁹⁾.

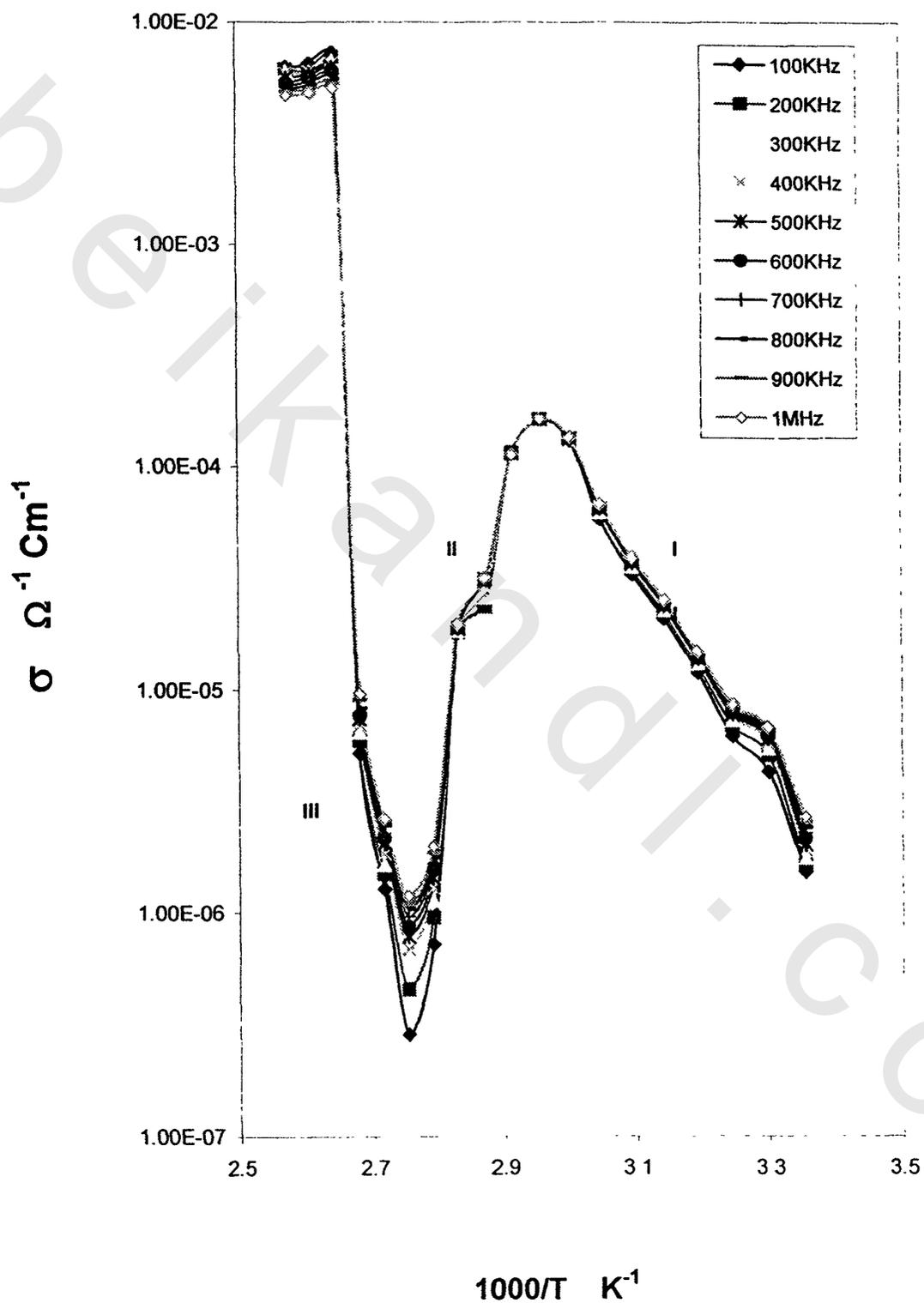


Figure (4.15): Variation of the AC conductivity as a function of temperature at different frequencies of Polyindene.

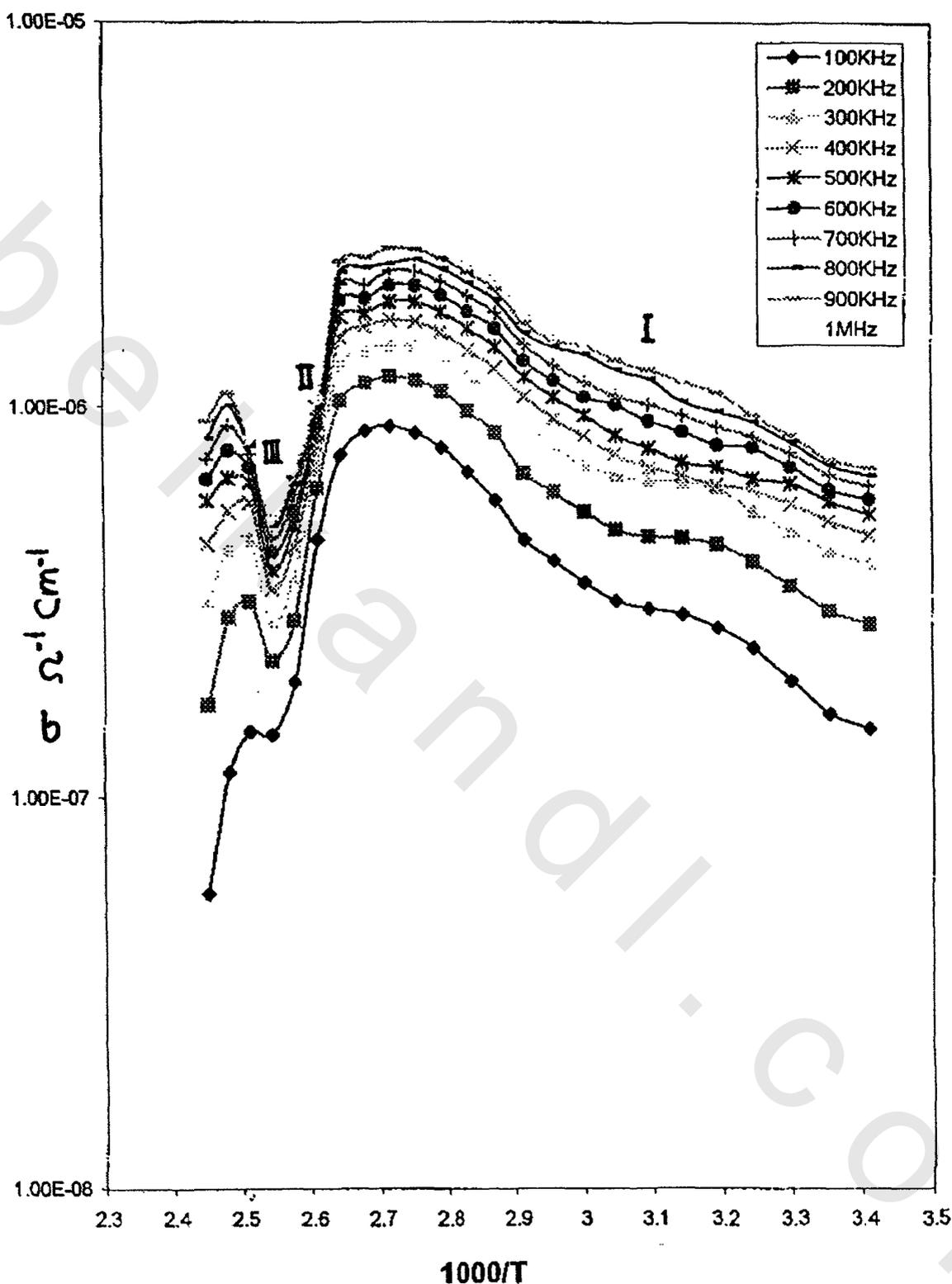


Figure (4.16): Variation of the AC conductivity as a function of temperature at different frequencies of Poly AN.

- **σ_{ac} Of Polyacrylonitrile PAN:**

The temperature dependence of the AC conductivity at different frequencies ranging from 100 KHz to 1 MHz for polyacrylonitrile is shown figure (4.16). From the figure it is clear that σ describes a similar behavior to that of PIn in the appearance of the four different regions of the conductivity.

In region I, there is a continuous increase of conductivity with the increase of the temperature which reaches a maximum at about 368 K. The increase in conductivity of PAN is may be attributed to the conjugation of the carbon-nitrogen system in the macromolecular chain ⁽³⁰⁾ and the lone pair of the electrons on the nitrogen atom makes the possible delocalization of the π -electrons with the σ -bond in the macrochain. It is thus assumed that the first step of conduction process is essentially due to the electronic conduction in co-operation with ionic one ⁽⁶⁰⁾.

In region II, the decrease of conductivity until reaches a minimum at temperature ≈ 393 K may also be attributed to a decrease in the number of the charge carriers due to thermal expansion of hopping paths.

In region III, the second step of conduction, which occurs at high temperatures, is may be due to the excitation of an electron from filled π -molecular orbital to lowest unfilled π -molecular orbital. Thus the electron is assumed to tunnel to ⁽⁶¹⁾ an equivalent empty level of a neighboring polymer segments in the anodic direction, whereas positive hole moves from polymer segments in the cathodic direction.

In region IV, the conductivity decreases again with increasing the temperature, due to the cession of the polymer main chain. This cession is accompanied by a decrease in the number of the charge carriers decreases leading to a decrease in the conductivity with increasing the temperature.

- **σ_{ac} of Polyacrylic acid PAA:**

Figure (4.17) correlates the temperature dependence of the AC conductivity of PAA at different frequencies ranging from 100 KHz to 1 MHz. From the curves, four regions are obtained similar to the two polymers PIn and PAN, but there are some observations of the curves in its behavior. It is clear that the broadening increase in region I which is limited by the temperature 343 K. The increase in the conductivity in this region is due to increasing the thermal energy which leads to the conjugation of the C=O system of the carboxylic group (due to the inductive effect of the C=O group) i.e. lead to the presence of two free electrons of the double bond on the oxygen atom. This increase in σ values at low temperature may correspond to semiconducting behaviour, since compounds with semiconducting

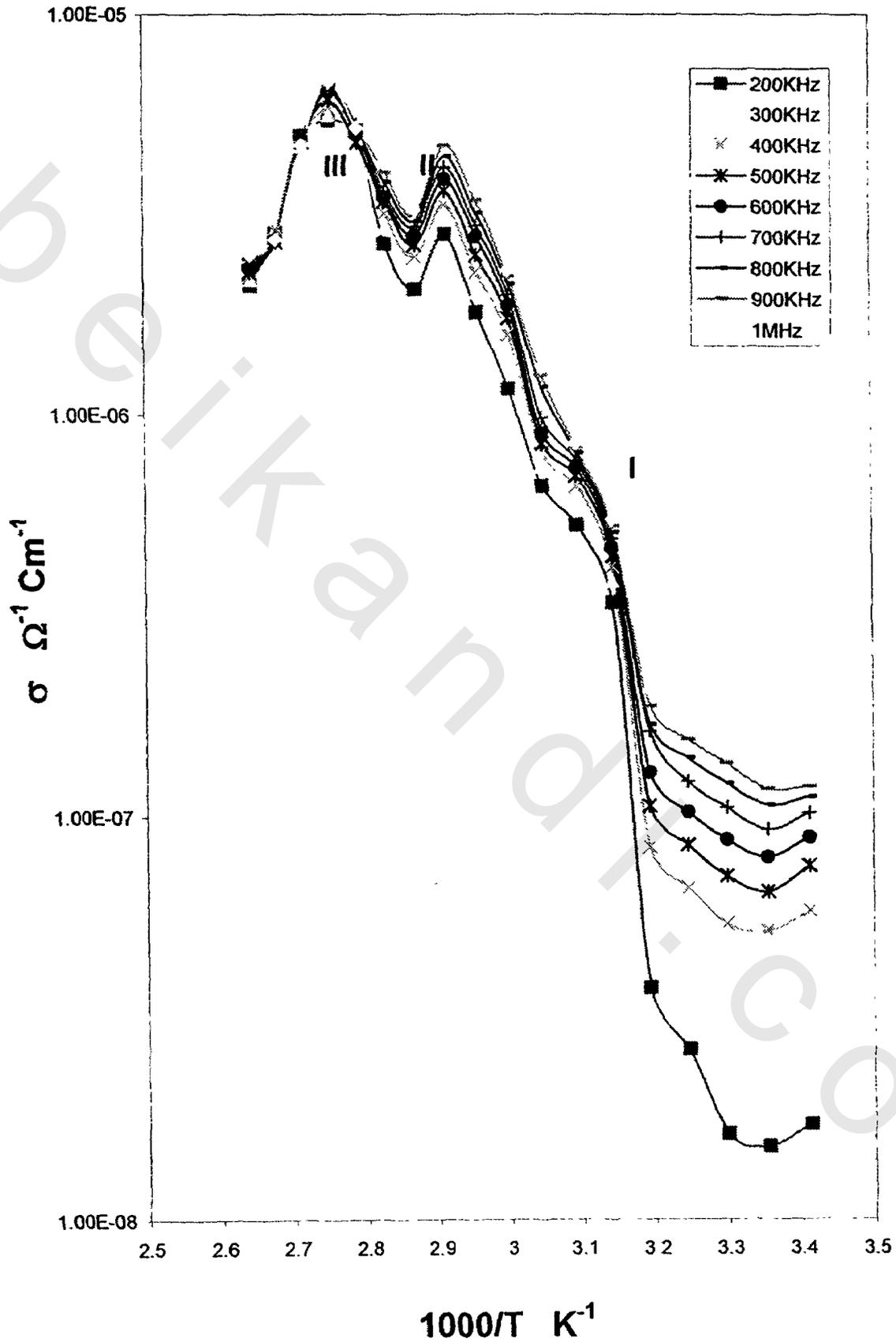


Figure (4.17): Variation of the AC conductivity as a function of temperature at different frequencies of Poly AA.

properties are characterized by electric conductivity ranged between 10^{-8} and 10^{-2} ($\Omega^{-1} \text{ cm}^{-1}$)⁽⁴⁶⁾.

In region II, this region take very short range of temperature and the decrease of the conductivity may be during the polymer decomposition and decarboxilation of some of the carboxylic groups of the polymer chain.

In region III, the conductivity increases again with increasing the temperature due to the thermal excitation which occurs as a result of increasing the number of the charge carriers resulting from the formation of π - bond in the main chain due to the decarboxylation. Thus the conduction process in the region is expected to be mainly electronic with hopping mechanism in which the electrons jumped from one localized state to another⁽⁶²⁾. In region IV, scission of the polymer main chain may be occurred, with similar behavior of PIn and PAN.

4.4.2. DC Conductivity of the homopolymers:

The temperature dependence of the DC electrical conductivity of the homopolymers is shown in figures (4.18 a, b, c). It is shown from the figures that the dc conductivity of each homopolymers has the same behavior as its ac conductivity. Also it is clear from the figures that the dc conductivity is lower than the ac conductivity, which confirm that the electrical conductivity increases with increasing the frequency.

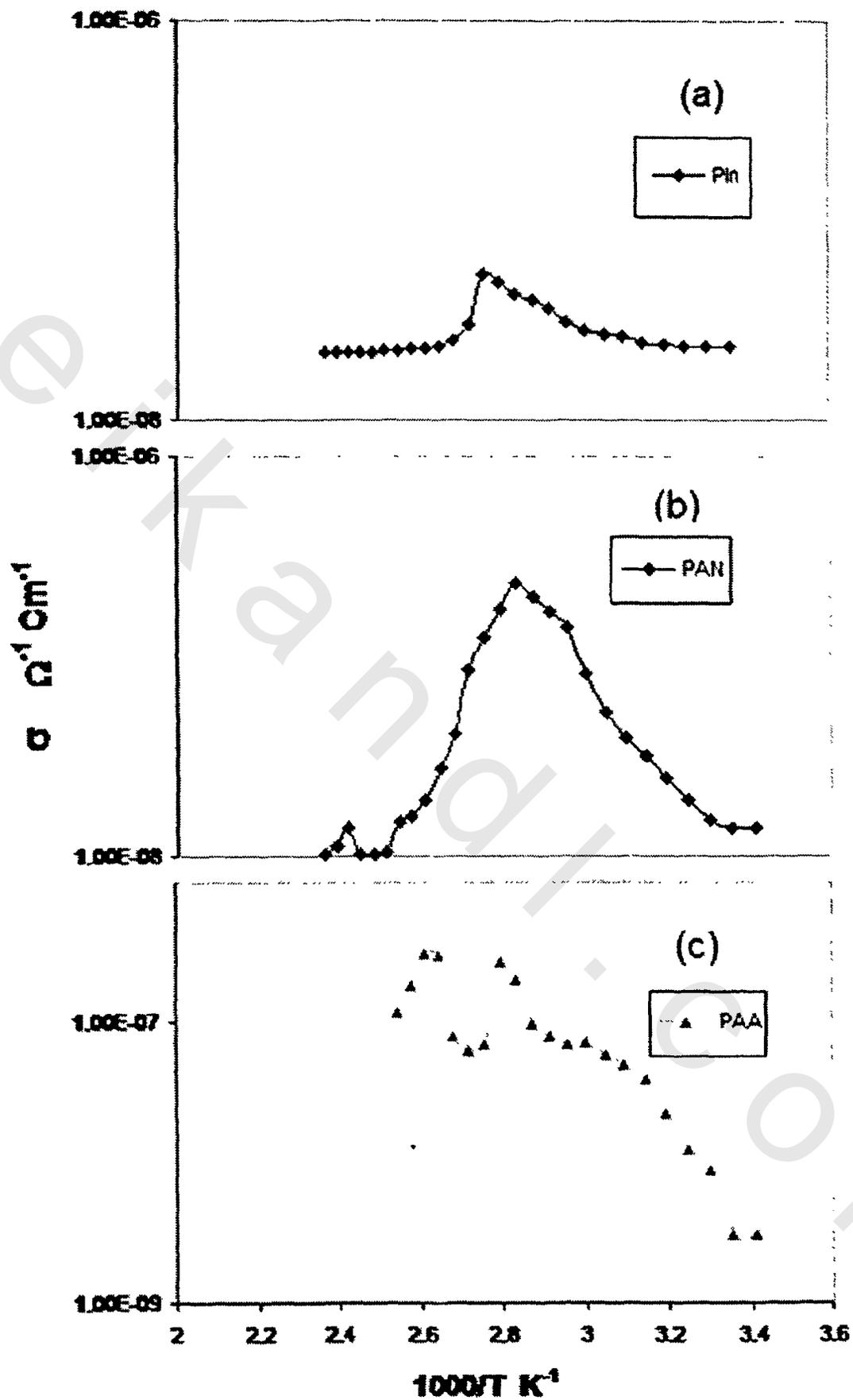


Figure (4.18): Temperature dependence of the dc conductivity of the homopolymers

Figure (4.18 a) shows that PIn posses the lowest values of the σ_{dc} except at 428 K where at this temperature PIn has highest value of σ_{dc} . Figure (4.18 b) shows the temperature dependence of the dc conductivity of PAN which give the highest values at two temperatures 353 and 398 K. This increase in the dc conductivity may be due to the charge carriers which move easily giving rise to a large current with an increase in the σ_{dc} .

Also, one can see the dependency of the dc conductivity on the temperature of PAA in figure (4.18 c). Increasing the σ_{dc} of PAA with temperature is attributed to the high polarity of the carboxylic (COOH) group which is rotating under the effect of the thermal energy.

The values of the activation energy for the different homopolymers ac and dc are listed in Table (4.11). The table displays the activation energy at the low temperature region E_1 and the high temperature region E_2 . From the final look of the table (4.11), one can see that there is a variance between the values of the activation energy of dc and ac conductivities, where dc has larger values than that of the ac one. The existence of the field which accompanies the different frequencies may be affected on decreasing the activation energy of the ac conductivity. In addition, it has been noticed that, as the field change with increasing frequencies the activation energy of the two regions decrease or at least stay stable as it is shown from the table (4.11).

Table (4.11): The activation energy values at different frequencies for the homopolymers in case of ac and dc conductivities in low (E_1) and high (E_2) temperature regions respectively.

F KHz	PIIn		PAN		PAA	
	E_1 eV	E_2 eV	E_1 eV	E_2 eV	E_1 eV	E_2 eV
DC	0.501	0.497	0.471	0.719	0.472	0.489
100	0.295	0.430	0.290	0.535	0.398	0.393
200	0.294	0.422	0.231	0.504	0.392	0.390
300	0.293	0.418	0.215	0.497	0.388	0.388
400	0.292	0.414	0.201	0.493	0.385	0.385
500	0.292	0.411	0.192	0.490	0.383	0.383
600	0.338	0.409	0.186	0.487	0.381	0.382
700	0.291	0.407	0.180	0.485	0.379	0.380
800	0.291	0.405	0.174	0.484	0.376	0.368
900	0.290	0.403	0.169	0.484	0.374	0.378
1000	0.290	0.401	0.167	0.484	0.372	0.377

4.4.3. AC Conductivity of the Copolymers:

- **In/AN Copolymers:**

The temperature dependence of the ac conductivity for the In/AN copolymers with different mol% is shown in figures (4.19)-(4.22). The temperature range of the measurements is between 293 and 448 K at different frequencies ranging from 100 KHz to 1 MHz for all samples. The figures show two activation energy regions for all samples except for the sample with mol% of the monomer concentration 70/30 which has only one activation energy for the high temperature region. The conductivity in the low temperature region is limited by temperature t_1 where behind it the conductivity begins to decrease. The value of t_1 is shifted towards higher temperatures gradually with increasing the mol% of AN in the monomer concentration, as shown in Table (4.12).

Table (4.12): The values of the temperatures t_1 (behind it the conductivity begin to decrease) t_2 (at which the conductivity begin to increase again) for the In/AN Copolymers.

In/AN mol%	t_1	t_2
20/80	378	433
30/70	368	423
50/50	348	388
70/30	363	408

This indicates that the AN rises the value of t_1 and this in accordance with that PAN has higher t_1 "368 K" than that of PIn "338 K". This increase in σ values at low temperature may correspond to semiconducting behaviour ⁽⁴⁶⁾.

The conductivity begins to increase again at temperature t_2 where its value decreases with decreasing the mol% of AN in the copolymer. The increase in the conductivity in this region indicates that degradation is expected to occur to the polymers due to increasing the thermal energy. Where, the high temperatures cause most polymers to degrade (depolymerization). In other polymers, the degradation occurs by a random breaking of bonds and formation of stable molecules with lower molecular weights. The higher the heat of polymerization, the lower is the tendency of the polymers to depolymerize.

The investigated polymers are difficult to be depolymerized because the heat of polymerization is higher than 60 KJ/mol ⁽⁶³⁾ (below which the polymer mainly degrades to monomer). However, they degrade by the abstraction of hydrogen atom from the main chain which is associated with the formation of radical. It is well known that the conduction in polymeric compounds occur via two

conduction mechanisms, ionic and electronic, depending on the nature of charge carriers existing within the network of the macromolecular chains. The formation of free radicals demonstrates the electronic conduction mechanism⁽⁶⁴⁾. Thus the increase in the conductivity values after the minimum can be explained by increase in the number of the charge carriers and within the polymer chain.

Figure (4.22) shows an anomalous behavior in the conductivity from the others. It can be seen that the stability region of the conductivity takes a long range of temperature until it reaches the second activation energy region. Thus the hopping model⁽⁶⁵⁾ is the most suitable model that describes the temperature independence behavior of conductivity.

Figure (4.23) shows a comparison between the ac conductivities of the In/AN copolymers at constant frequency (200 KHz) for all the samples. It is shown from the figure that the ac conductivity of the In/AN copolymers decreases as the mol% of the indene in the monomer concentration increases.

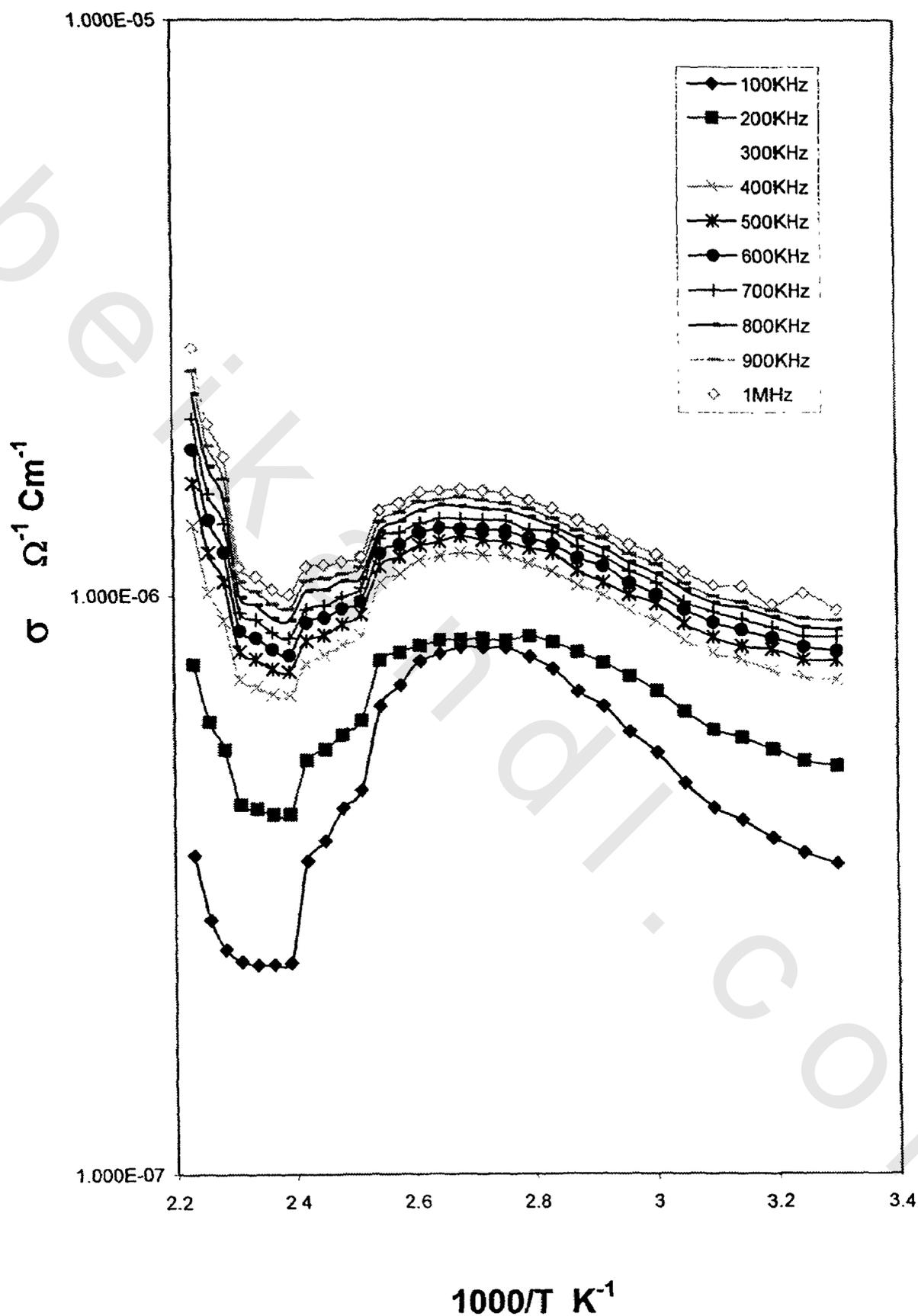


Figure (4.19): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AN of 20/80 mol%.

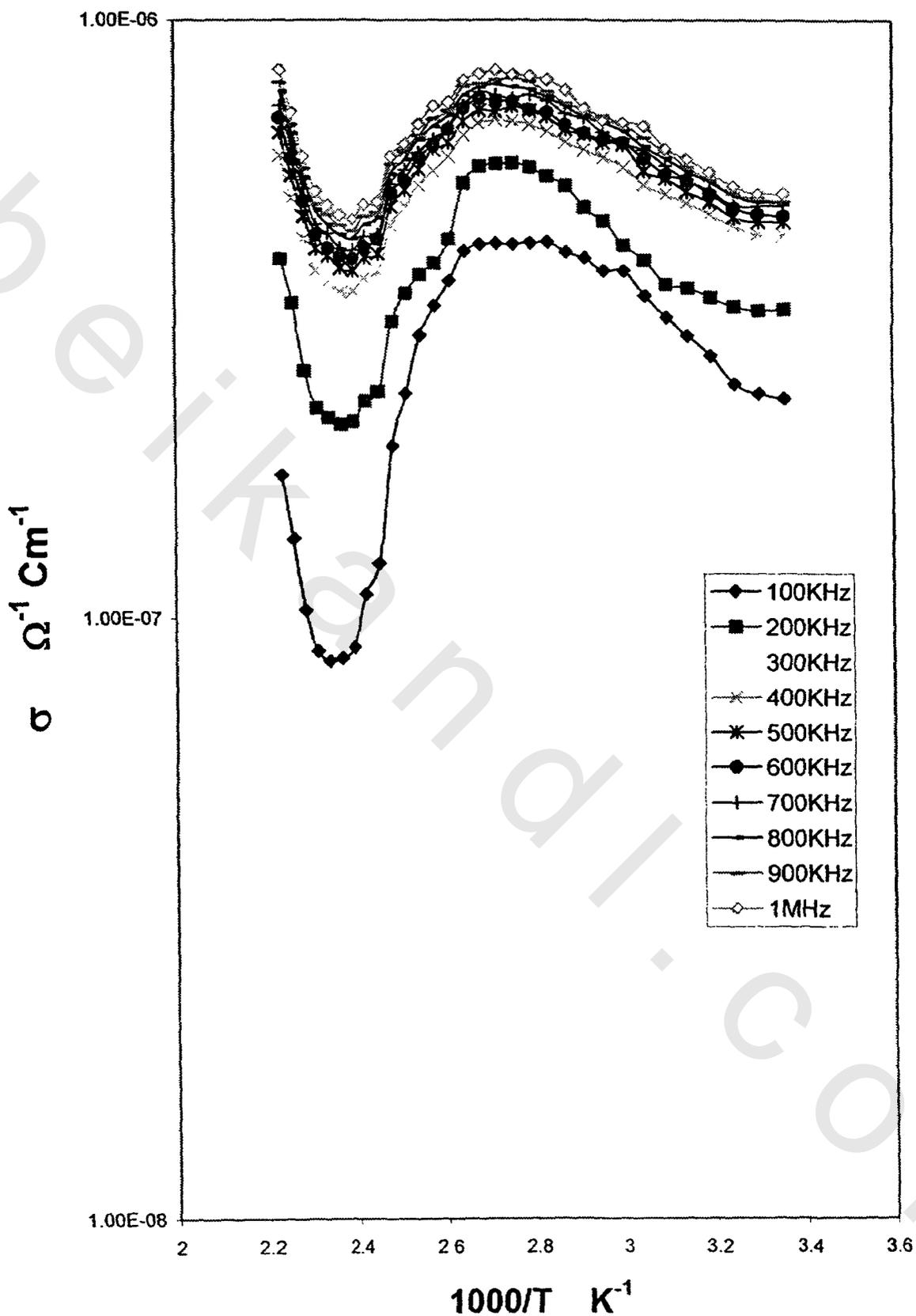


Figure (4.20): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AN of 30/70 mol%.

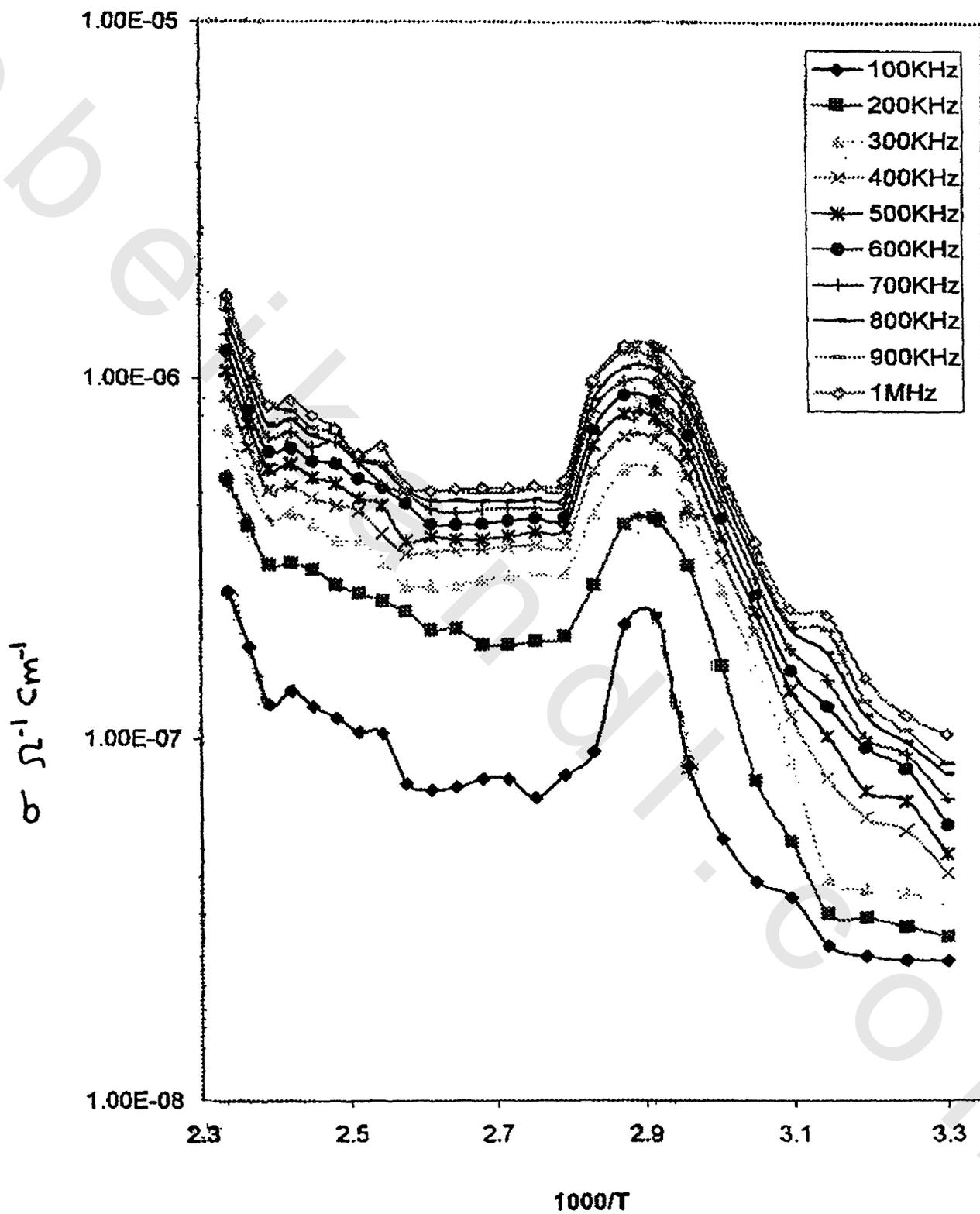


Figure (4.21): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AN of 50/50 mol%.

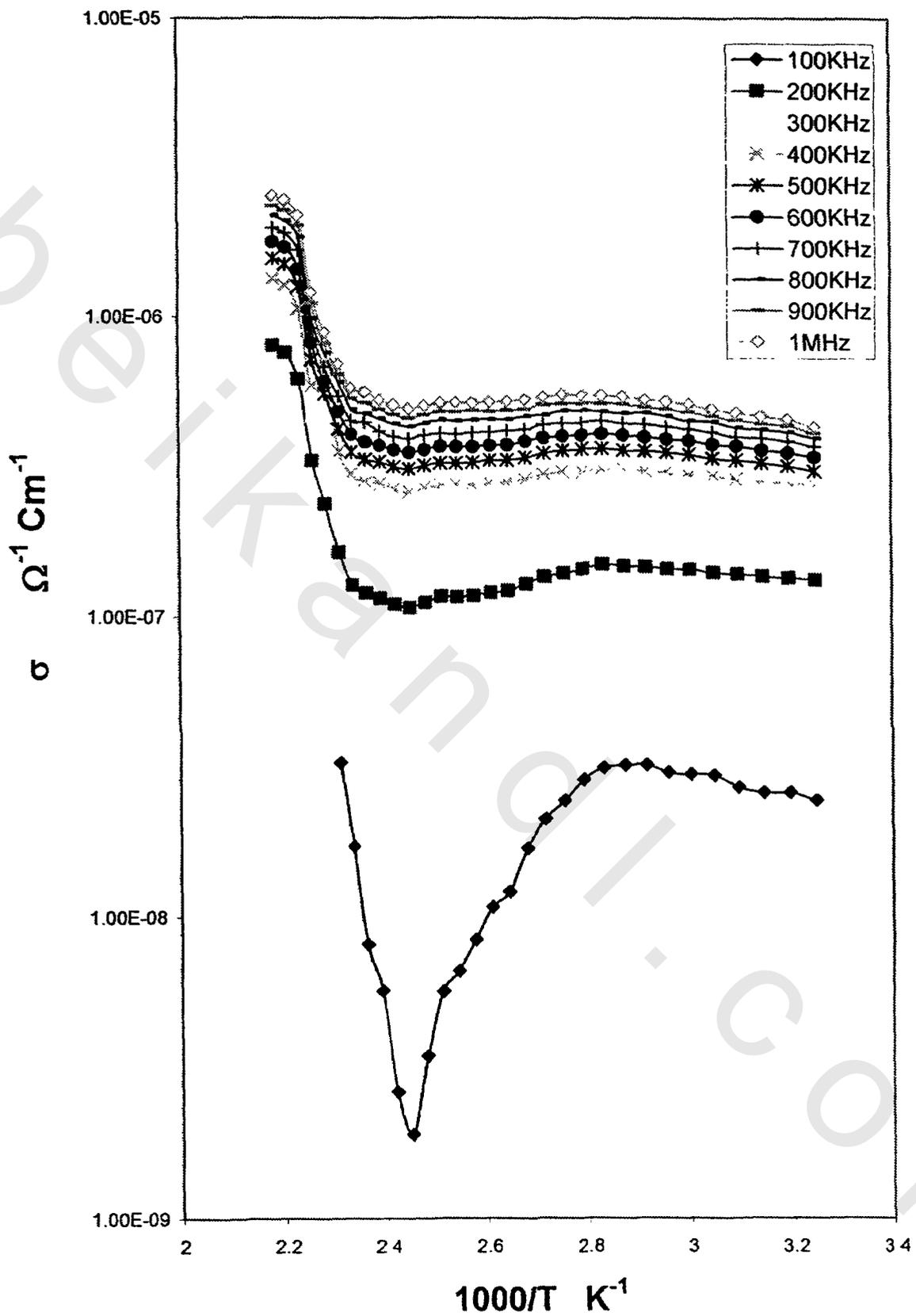


Figure (4.22): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AN of 70/30 mol%.

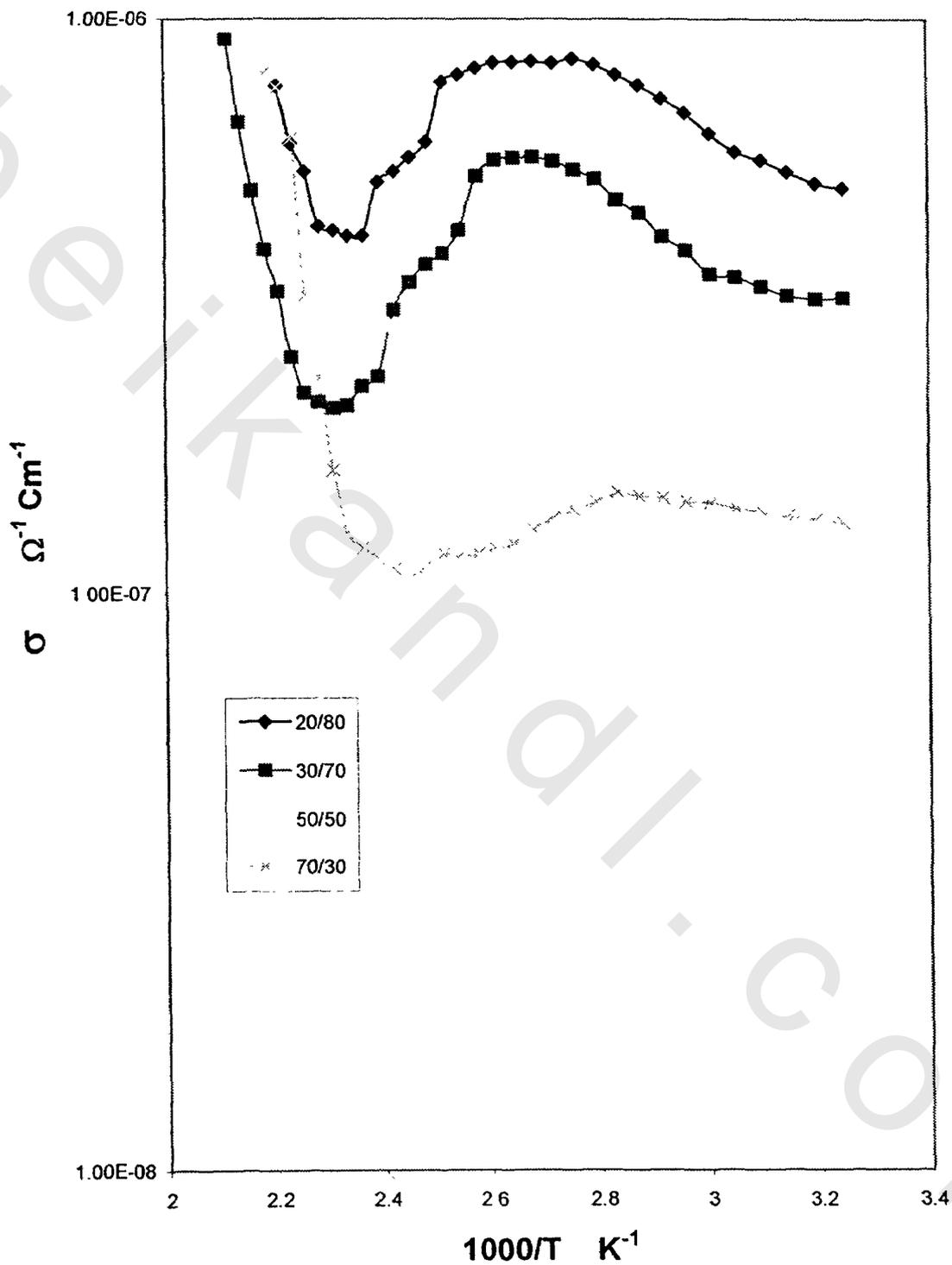


Figure (4.23): Comparison between the ac conductivities of the In/AN copolymers at 200 KHz.

However the ac conductivity of the homopolymers shows that Polyindene has higher values of the ac conductivity than that of PAN. This may be due to the rearrangement of the bonds which occurs during copolymerization attended to weakness of the compound bonds without changing in the charge carriers' velocity leading to decrease in the conductivity with increasing the mol% of the indene in the monomer concentration.

- **In/AA Copolymers:**

The variation of the AC conductivity of In/AA copolymers has been studied over the temperature range 393 to 473 K and the frequency range from 100 KHz to 1MHz and is shown in the figures (4.24) to (4.27). It is shown from the figures that the conductivity of the In/AA copolymers shows similar behavior to that of the conductivity of the In/AN copolymers in the presence of the two linear dependence of the conductivity at the low and high temperatures. It is shown from the figures that the conductivity increases sharply for all the samples until it reaches a certain value after which the conductivity begins to decrease. The increase in σ values at low temperature may correspond to semiconducting behaviour⁽⁶⁶⁾.

The values of t_1 are fixed for all frequencies of all the samples except for the sample of 50/50 mol% for which the value of t_2 is shifted to lower temperature by increasing the frequency, as shown in Table (4.13).

This can be explained as follow: increasing the frequency of the applied field will increase the disordering of the dipoles ⁽⁶⁷⁾ and thus causes this shift in the temperature t_2 by increasing the frequency.

Table (4.13): The values of the temperatures t_1 (behind it the conductivity begin to decrease) t_2 (at which the conductivity begin to increase again) for the In/AA Copolymers.

In/AA mol%	t_1	t_2
20/80	413	438
30/70	403	413
50/50	373	363 - 438
70/30	338	358

Then at temperature t_2 the conductivity begins to increase again with increasing the temperature. Also similar to In/AN copolymers the In/AA copolymers degrade by the abstraction of hydrogen atom from the main chain which is associated with the formation of radical. The formation of free radicals demonstrates the electronic conduction mechanism ⁽⁶⁴⁾. Thus the increase in the conductivity values after the minimum can be explained by increase in the number of the charge carriers and within the polymer chain.

Figure (4.28) shows a comparison between the ac conductivities of the In/AA copolymers at fixed frequency for all the samples. It is shown from the figure that the ac conductivity of the In/AA copolymers increases as the mol% of the indene in the monomer concentration increases. This behaviour is in accordance with that Polyindene has higher ac conductivity than PAA.

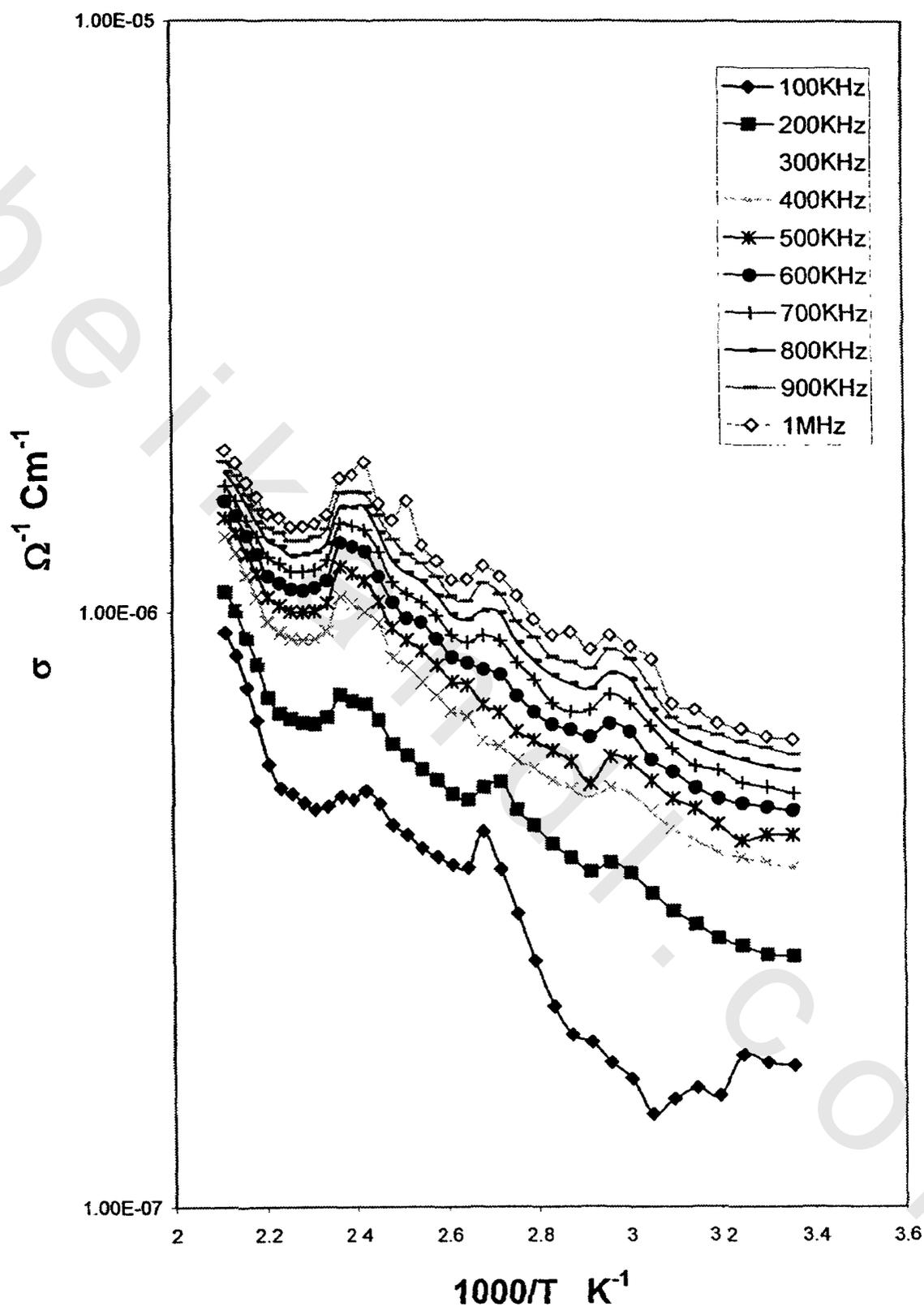


Figure (4.24): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AA of 20/80 mol%.

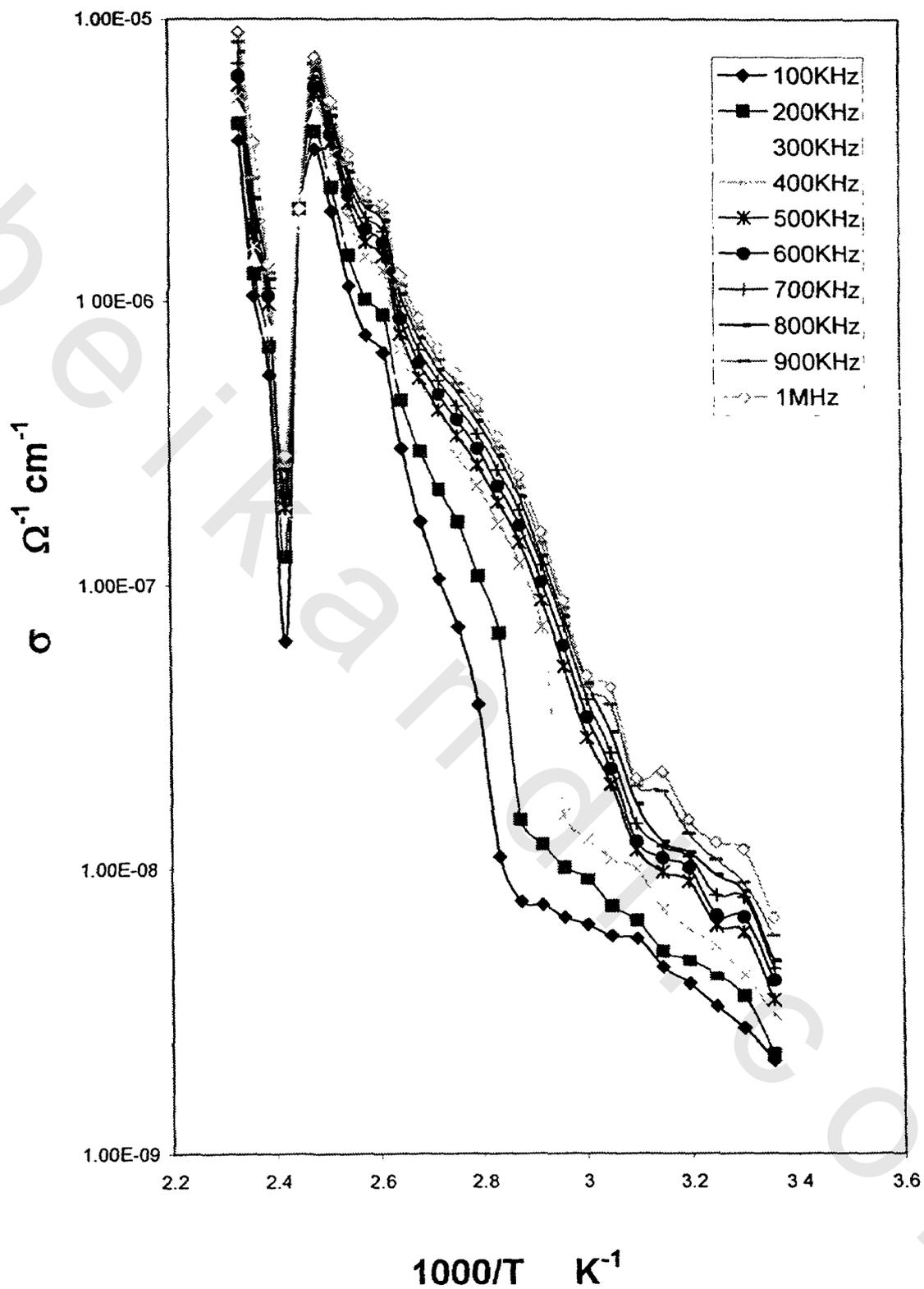


Figure (4.25): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AA of 30/70 mol%.

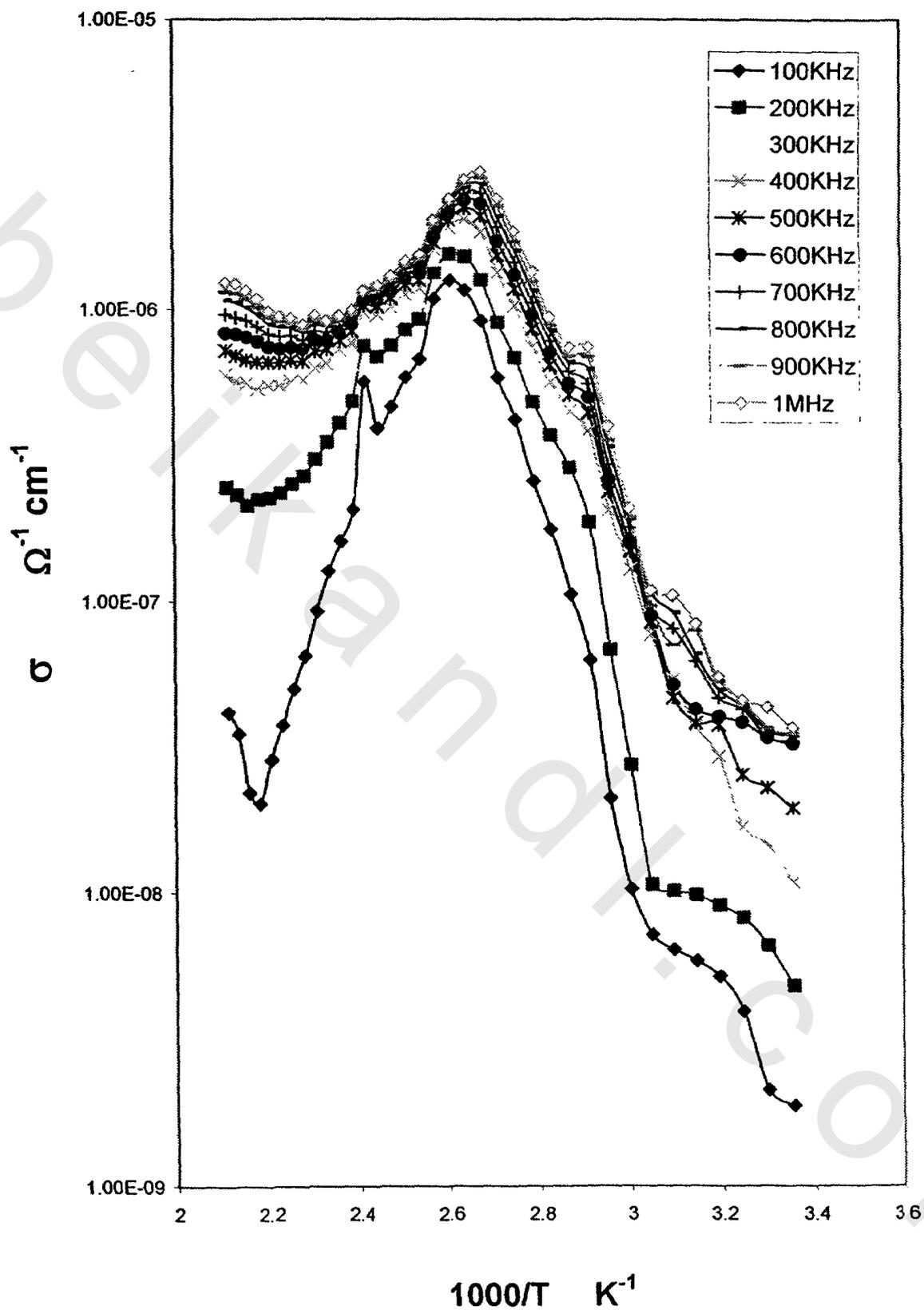


Figure (4.26): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AA of 50/50 mol%.

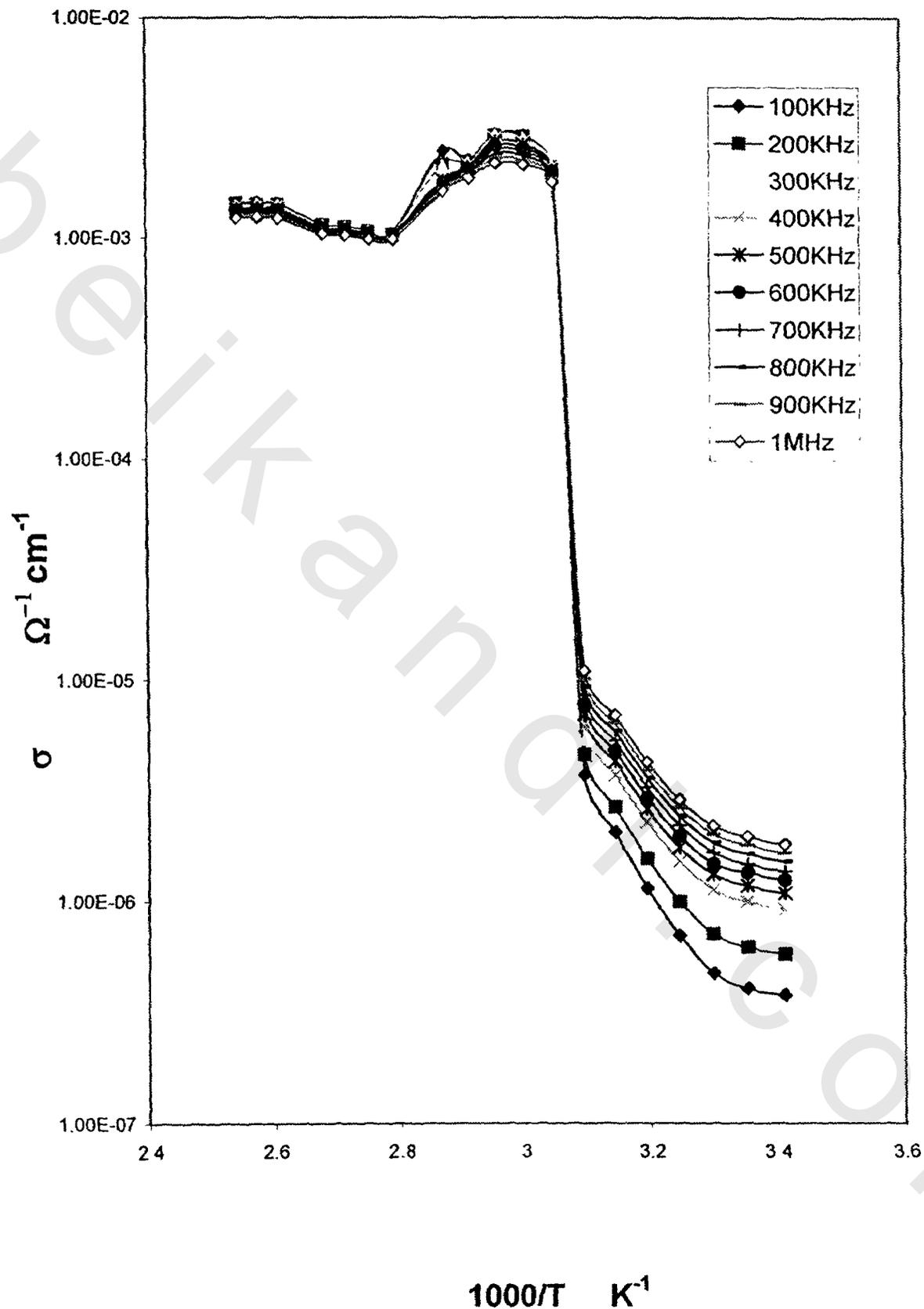


Figure (4.27): Variation of the AC conductivity as a function of temperature at different frequencies for In-co-AA of 70/30 mol%.

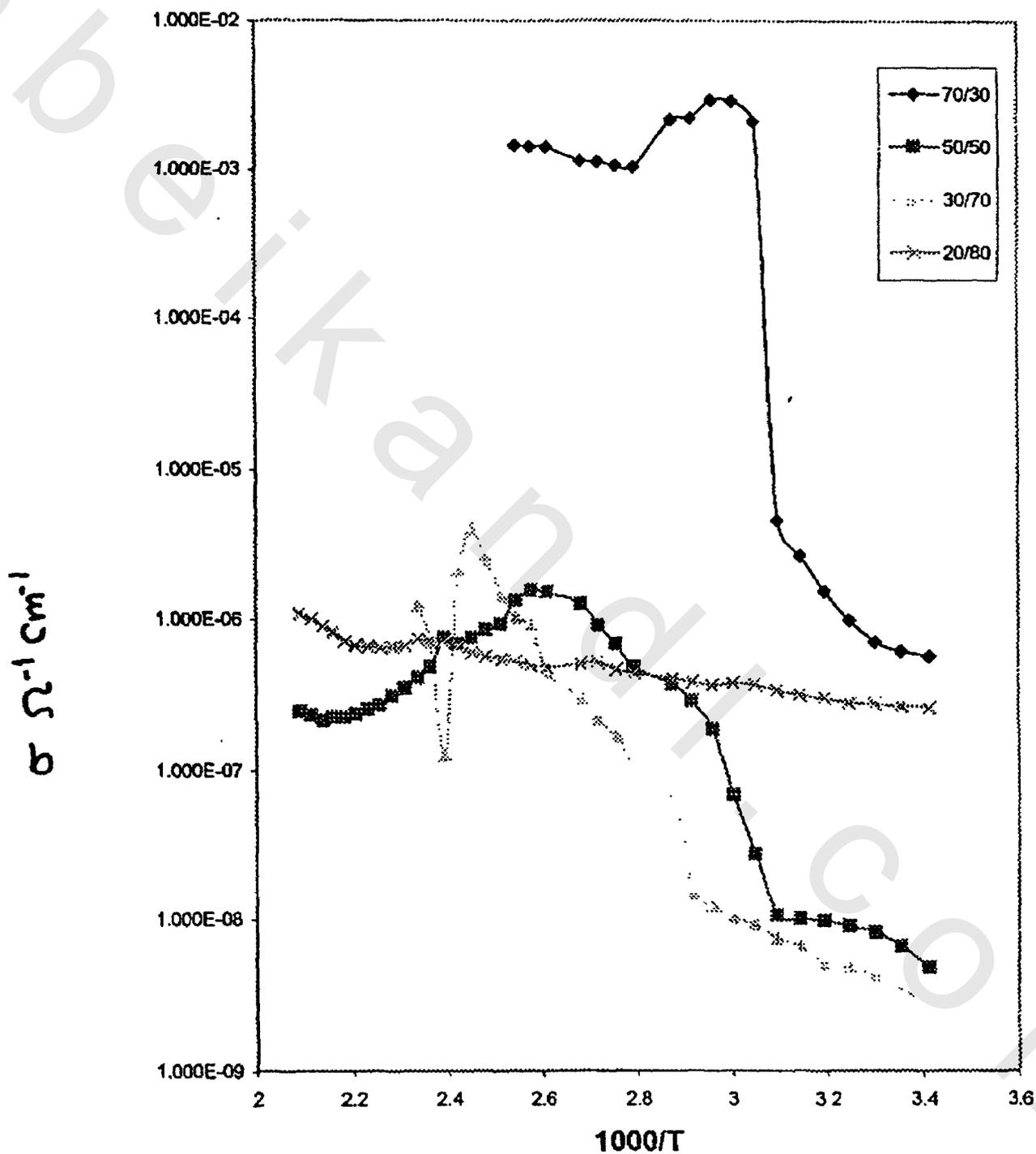


Figure (4.28): comparison between the ac conductivities of the In/AA copolymers at 200 KHz.

4.4.4. DC Conductivity of the Copolymers:**• In/AN Copolymers:**

The appearance of dc conductivity for In/AN copolymers is shown in figure (4.29), where a comparison between the different samples of In/AN copolymers with different mol% of the copolymer compositions and its dependence on the reciprocal of the temperature takes place. It is noted from the figure that each sample has a similar behavior of increasing and decreasing the dc conductivity similar to the ac one.

It is also shown from the figure that the dc conductivity increases with increasing the mol% of the AN in the copolymer composition, with the exception of sample of 50/50 mol% which has different behavior with respect to the other and possesses a highest conductivity values. This may be attributed to the equality appearing in the molar ratio.

The values of the activation energy of the In/AN copolymers with the different mol% of the copolymers of 20/80, 30/70, 50/50 and 70/30 respectively in case of dc and ac conductivities at the low (E_1) and high (E_2) temperature regions are listed in Table (4.14).

Table (4.14): Values of the activation energy (in eV) of In/AN copolymers for different frequencies in case of dc and ac conductivities at low (E_1) and high (E_2) temperature regions respectively.

	20/80		30/70		50/50		70/30
F KHz	E_1 eV	E_2 eV	E_1 eV	E_2 eV	E_1 eV	E_2 eV	E_2 eV
DC	0.513	0.664	0.509	0.682	0.467	0.640	0.692
100	0.410	0.573	0.413	0.596	0.487	0.565	0.665
200	0.402	0.543	0.408	0.566	0.459	0.536	0.580
300	0.397	0.532	0.401	0.556	0.438	0.525	0.558
400	0.394	0.523	0.399	0.551	0.432	0.518	0.549
500	0.392	0.517	0.398	0.548	0.428	0.512	0.543
600	0.391	0.512	0.397	0.545	0.424	0.508	0.538
700	0.390	0.508	0.396	0.543	0.421	0.504	0.534
800	0.388	0.504	0.396	0.542	0.418	0.501	0.530
900	0.388	0.500	0.395	0.540	0.417	0.497	0.527
1000	0.386	0.497	0.394	0.538	0.415	0.496	0.525

The Table indicates that the activation energy values of the two regions decrease with increasing the frequency. It is also shown that the second activation energy region E_2 is almost higher than that of the first region E_1 . This is due to the higher dissociation energy needed to form the charge carriers for the intrinsic conduction ⁽⁶⁸⁾. In addition, it has been noticed that the activation energy of the dc conductivity for the two regions is higher than that of the ac, because of the existence of the electric field related to every frequency affected on the charge carriers' mobility as well as decreasing the ac activation energy. From the above table, one can see that the sample of 70/30 mol% has no low activation energy values; this may be due to the stability which takes places on the sample conductivity with increasing the temperature, which is attributed to the stability of moving the charge carriers.

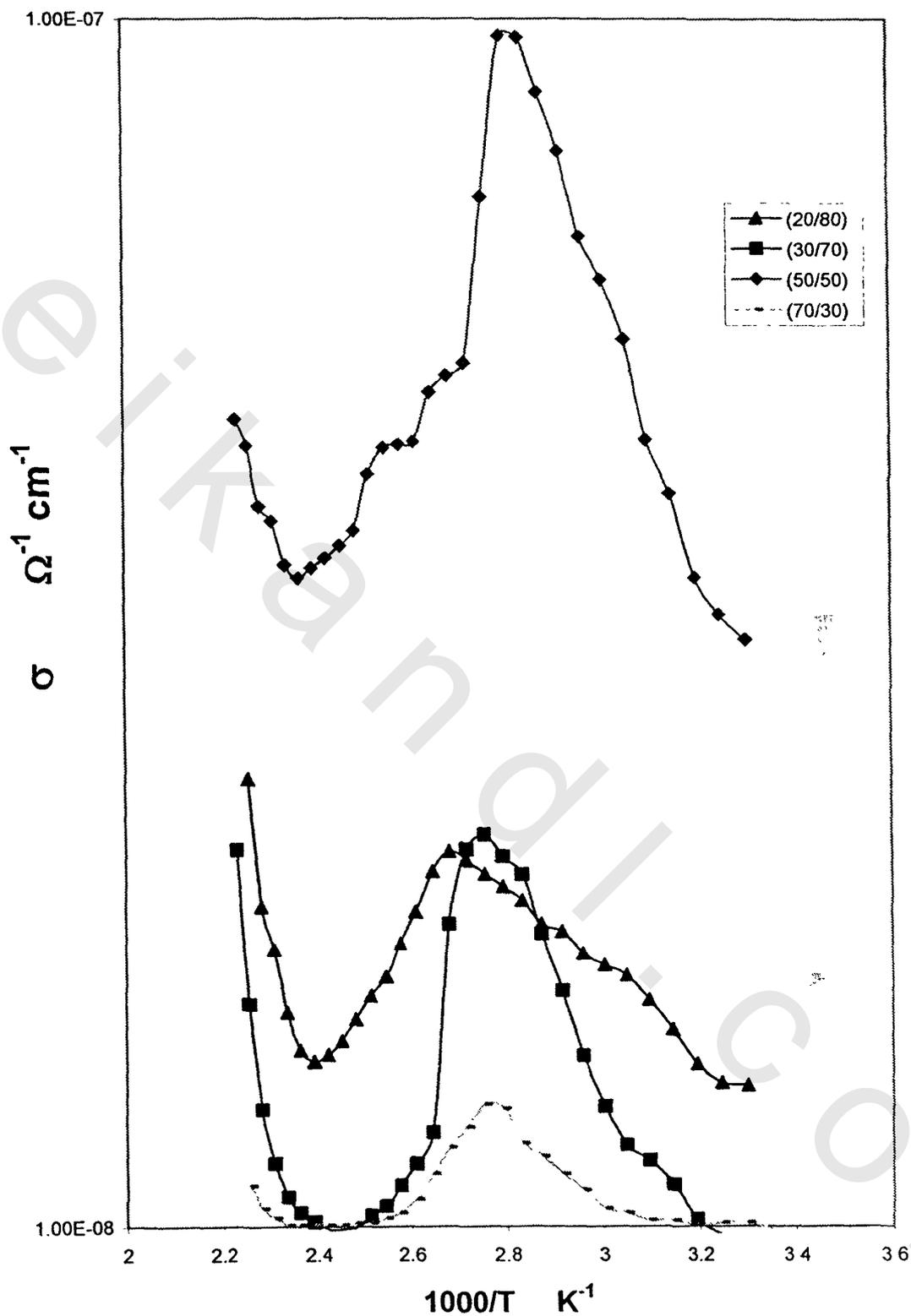


Figure (4.29): Temperature dependence of the dc conductivity of the In/AN copolymers with different molar ratios.

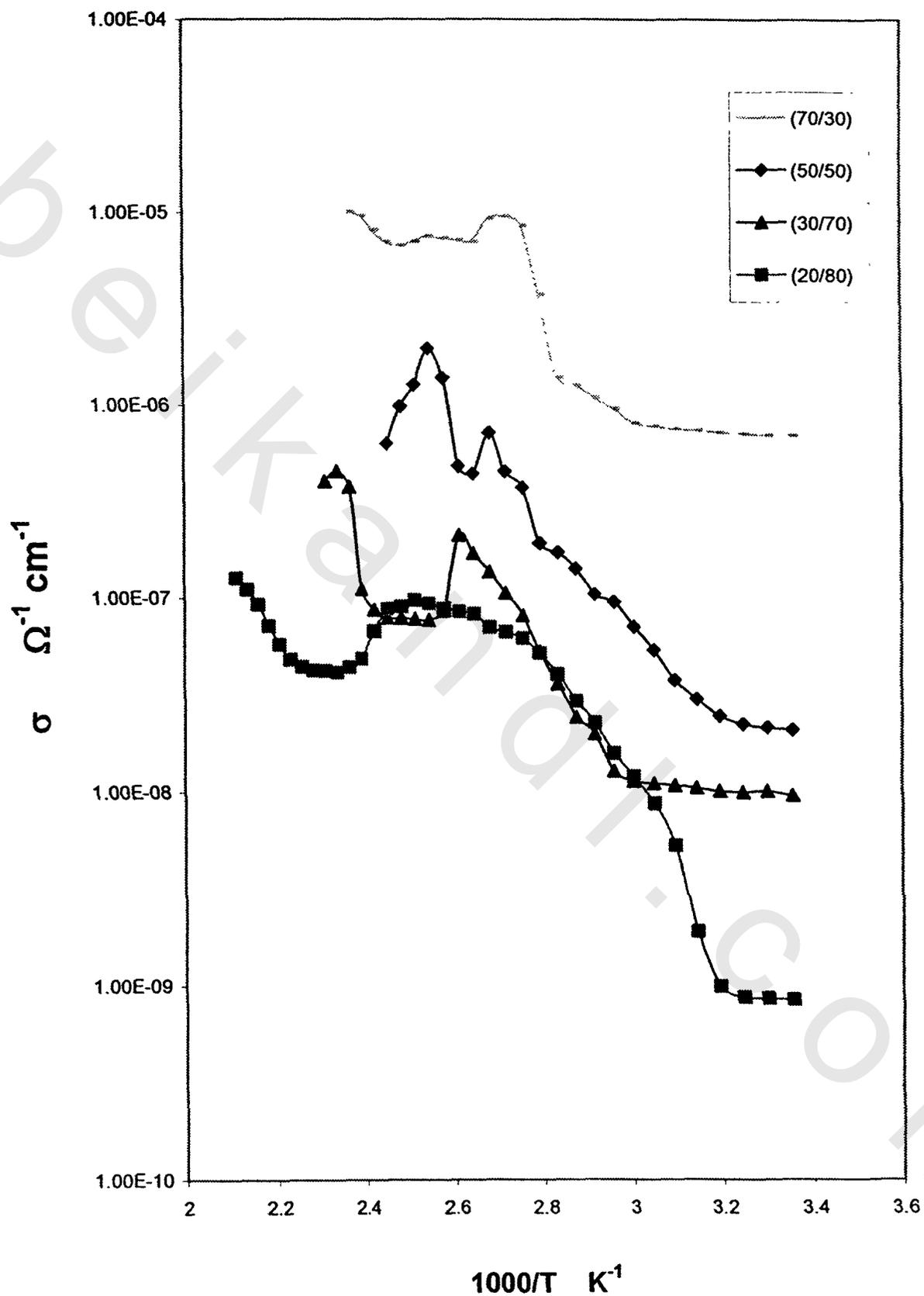


Figure (4.30): Temperature dependence of the dc conductivity of the In/AA copolymers with different molar ratios.

- **In/AA Copolymers:**

Figure (4.30) correlates the temperature dependence of the dc conductivity of the In/AA copolymers with different mol% of the copolymer composition. It is shown from the figure that each sample has a similar behavior of the dc conductivity as its ac one. The figure investigates that the dc conductivity also increases with increasing the mol% of indene in the copolymer. This behaviour is in accordance with the ac conductivity where figure (4.28) shows the increasing the ac conductivity with increasing the mol% of the indene in the copolymer.

The values of the activation energy of the In/AA copolymers with the different mol% of the copolymers of 20/80, 30/70, 50/50 and 70/30 respectively in case of dc and ac conductivities at the low (E_1) and high (E_2) temperature regions are tabulated in Table (4.15).

There is no obvious change in both the activation energy values of dc and ac. On the other hand, one can see that the activation energy of the two regions slightly decreases with increasing the frequency as a result of changing the electric field accompanied to each frequency as well as the movement of the charge carriers.

Table (4.15): Values of the activation energy (in eV) of In/AA copolymers for different frequencies in case of dc and ac conductivities at low (E_1) and high (E_2) temperature regions respectively.

F KHz	20/80		30/70		50/50		70/30	
	E_1 eV	E_2 eV						
DC	0.459	0.554	0.524	0.557	0.408	0.381	0.529	0.571
100	0.461	0.562	0.508	0.518	0.469	0.695	0.367	0.216
200	0.441	0.554	0.485	0.507	0.448	0.615	0.359	0.216
300	0.437	0.548	0.475	0.500	0.440	0.591	0.353	0.217
400	0.433	0.544	0.468	0.497	0.435	0.578	0.349	0.217
500	0.431	0.541	0.464	0.495	0.430	0.570	0.345	0.218
600	0.427	0.538	0.459	0.491	0.427	0.564	0.342	0.218
700	0.424	0.535	0.456	0.488	0.424	0.558	0.339	0.218
800	0.421	0.533	0.453	0.484	0.422	0.554	0.336	0.219
900	0.419	0.531	0.450	0.481	0.420	0.551	0.334	0.220
1000	0.416	0.529	0.447	0.477	0.418	0.548	0.332	0.221

4.5. Dielectric properties of the polymers:

A characteristic feature of polymers is the independent movement of chain sections consisting a large number of monomeric units (segments). Besides segments, smaller and more mobile kinetic units are also moving in polymers. Such kinetic independent units may be side chains or individual atomic groups e.g. polar substituents. The relaxation time of the orientation moment of such groups is smaller than the relaxation time of the main chain segments and for this reason they can retain their mobilities at lower temperatures, where the segments of the main chain are practically immobile. If a polymer containing polar groups is placed in an electric field, orientation of its segments and smaller kinetic units will be observed at definite relaxation time to the field frequency ratios and this give rise to definite values of dielectric constant and dielectric loss.

Two types of dielectric loss have been established for all polymers. The first type called dipole-segmental, is associated with orientation rotation of the polar units of the macromolecules (α -relaxation), (above T_g). The second type, called dipole-group, is due to the orientation of the polar groups themselves (β, γ, \dots relaxation), (above and below T_g of the polymers).⁽⁴⁾

4.5.1. The Electrical Permittivity of the homopolymers:

- **ϵ' for the Polyindene PIn:**

Fig (4.31) shows the temperature dependence of the real part of the relative permittivity ϵ' for PIn at different frequencies ranging from 100 KHz to 1 MHz and in the temperature range from 293 to 403 K. From the figure, it can be seen that the value of the real part of the permittivity ϵ' increases sharply with temperature and give a strong relaxation peak at about temperature ≈ 328 K. After this relaxation peak, the value of ϵ' decreases and then increases again with increasing the temperature and give another relaxation peak at 348 K. At relatively lower temperature, the orientation of the dipoles is facilitated which may be attributed to rearrangement of the chain and this leads to an increase in the value of the dielectric constant ϵ' with increasing temperature. Increasing the temperature after the first peak will increase the thermal energy given to the dipoles which disturbs their orientation, so that the orientational electric dipole moment as well as the dielectric constant decreases with increasing the temperature given to the dipoles. At higher temperature, the value

of ϵ increases again and reaches a second relaxation peak. This is mainly due to chain melting (the chain melting does not mean the decomposition of the compound), which leads to the increase in polarization arising from the motion of chain segments and their orientation in the direction of the applied electric field⁽⁶⁹⁾.

From figure (4.31), one can observe that ϵ decreases with increasing the frequency. This may be due to the electric dipoles which are no longer able to rotate sufficiently fast to follow the field variations. This will lead to a decrease in the dielectric constant with increasing the frequency. This phenomenon is known as anomalous dielectric dispersion.

- **ϵ for the Polyacrylonitrile PAN:**

The variation of the dielectric constant with the temperature measured in the frequency range from 100 KHz to 1 MHz and in the temperature range from 293 to 413 K for PAN is shown in figure (4.32). The figure indicates the appearance of two peaks; the most significant peak is the maximum peak which arises around the temperature ≈ 368 °K, for all the frequencies. It is certain that the orientation of the nitrile groups causes this strong relaxation. Because the nitrile groups are directly bounded to the polymer backbone, the movement of the nitrile groups is very likely correlated to the movement of the polymeric backbone⁽⁷⁰⁾. The other relaxation peak is at 318 K, this may be due to the combined effect of the high frequency field and the increase of the thermal energy which affected on the orientational dipoles of the polymer. It is also investigated that

ϵ' of PAN is inversely dependent on the frequency. At 333 K there is a third relaxation process existing at higher frequencies.

- **ϵ' for the Polyacrylic Acid PAA:**

Figure (4.33) correlates the temperature dependence of the real part of the permittivity ϵ' for PAA at frequency ranging from 100 KHz to 1 MHz. It is clear that ϵ' describes a similar behavior to that of PIn in the appearance of two relaxation peaks, with an exception of the maximum temperature, the first peak obtained at 340 °K, and the second peak at 358 °K. Also the observed behavior of ϵ' for PAA with the frequency is also similar to that of PIn (inversely dependent on the frequency). However the values of ϵ' for PAA are ranging from 0 to 25 which are lower than that of PIn and higher than that of PAN. These higher values of ϵ' may be due to the heterocyclic structure possessed to PIn. PAA has higher values of ϵ' than that of PAN due to the higher polarity of PAA than that of PAN. Also, there is a third peak which looks like shoulder observed at high temperature, but it is disappeared with increasing the frequency and this may be due to the external field accompanied with every frequency which effected on the orientational dipoles existing on the PAA sample.

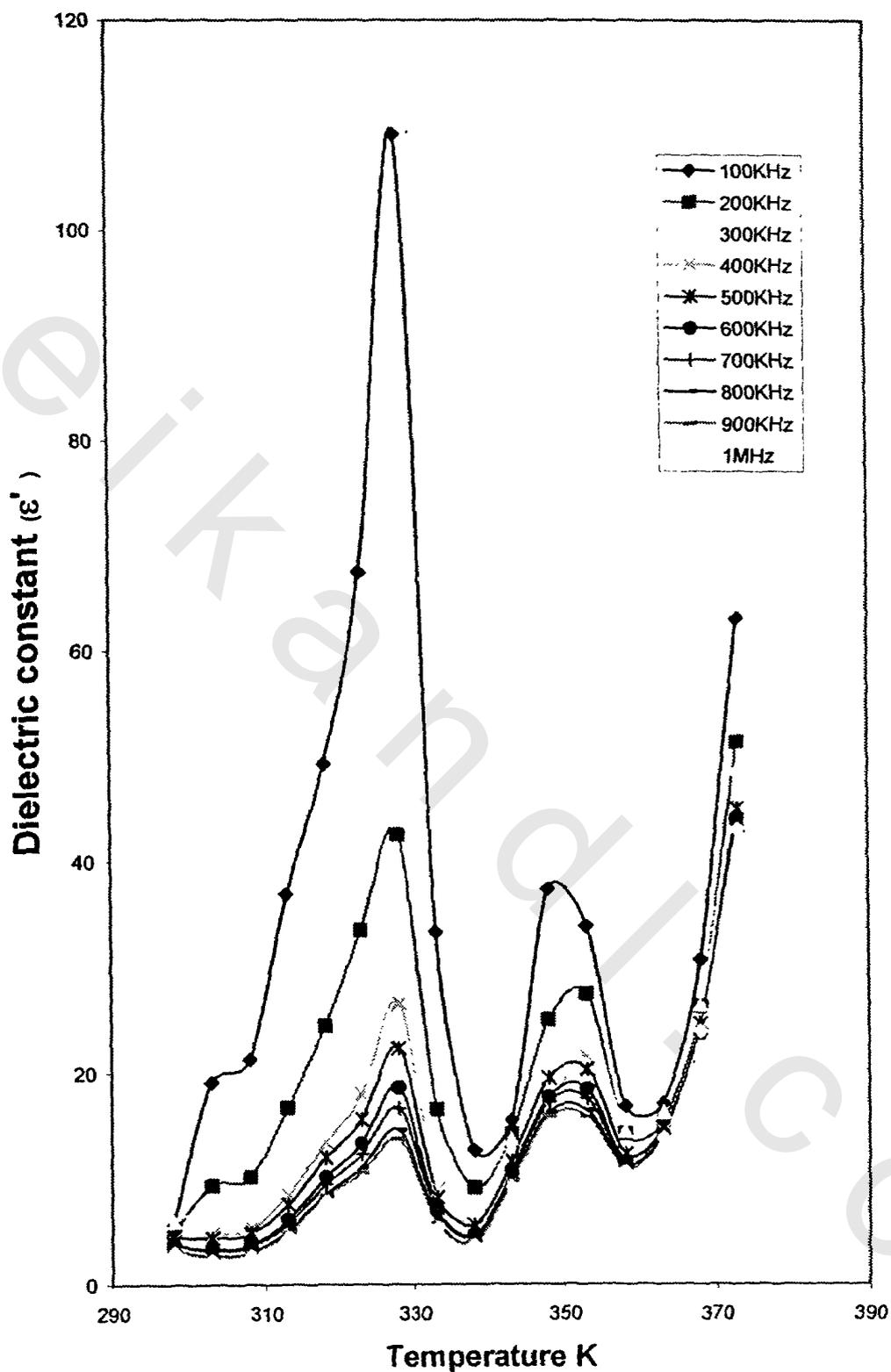


Figure (4.31): Variation of the dielectric constant as a function of temperature at different frequencies for Polyindene.

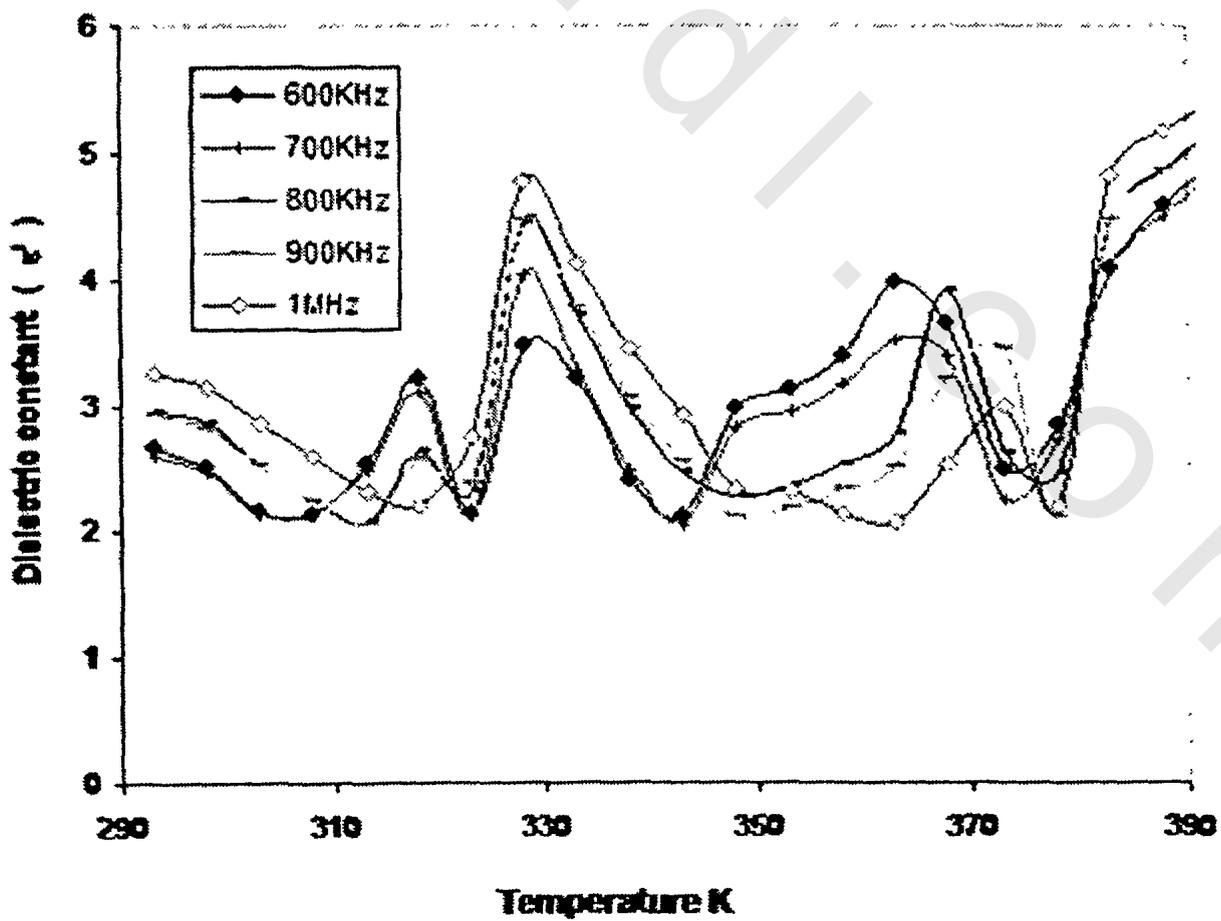
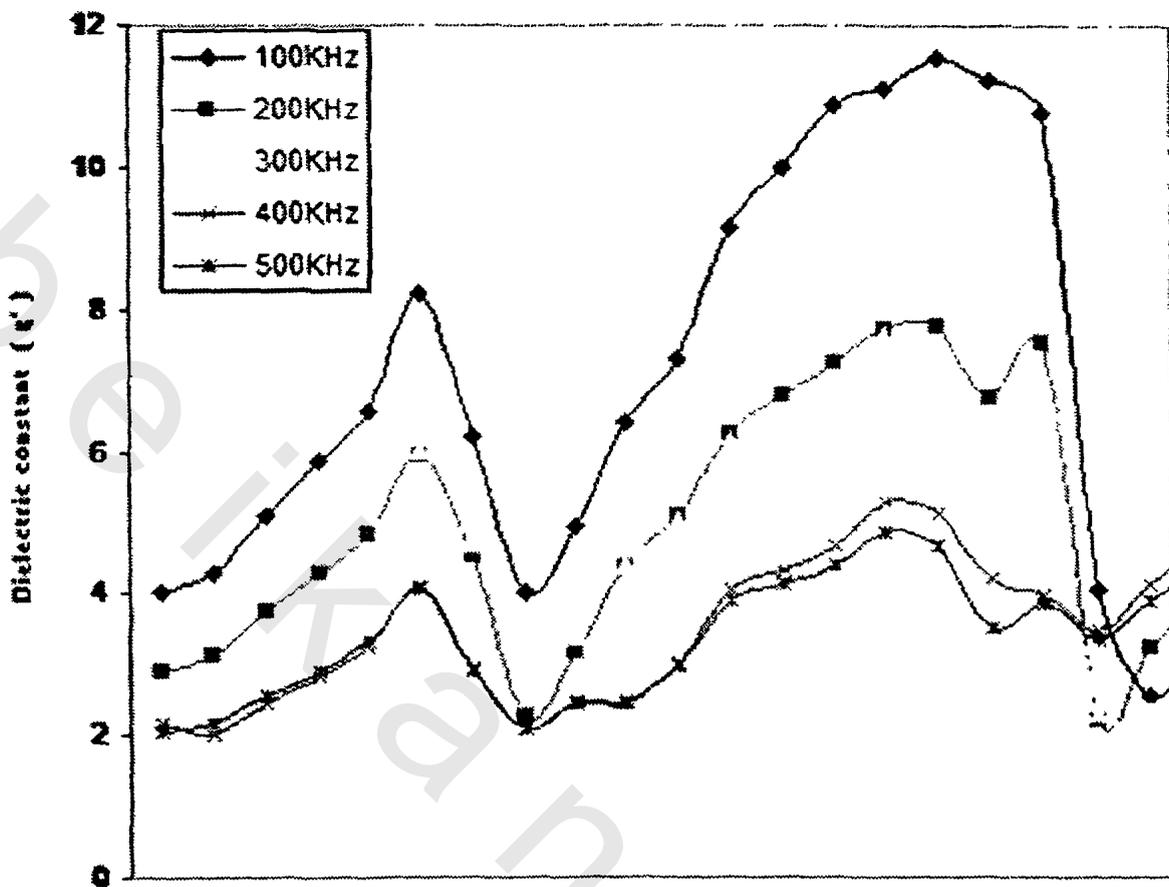


Figure (4.32): Variation of the dielectric constant as a function of temperature at different frequencies for PAN.

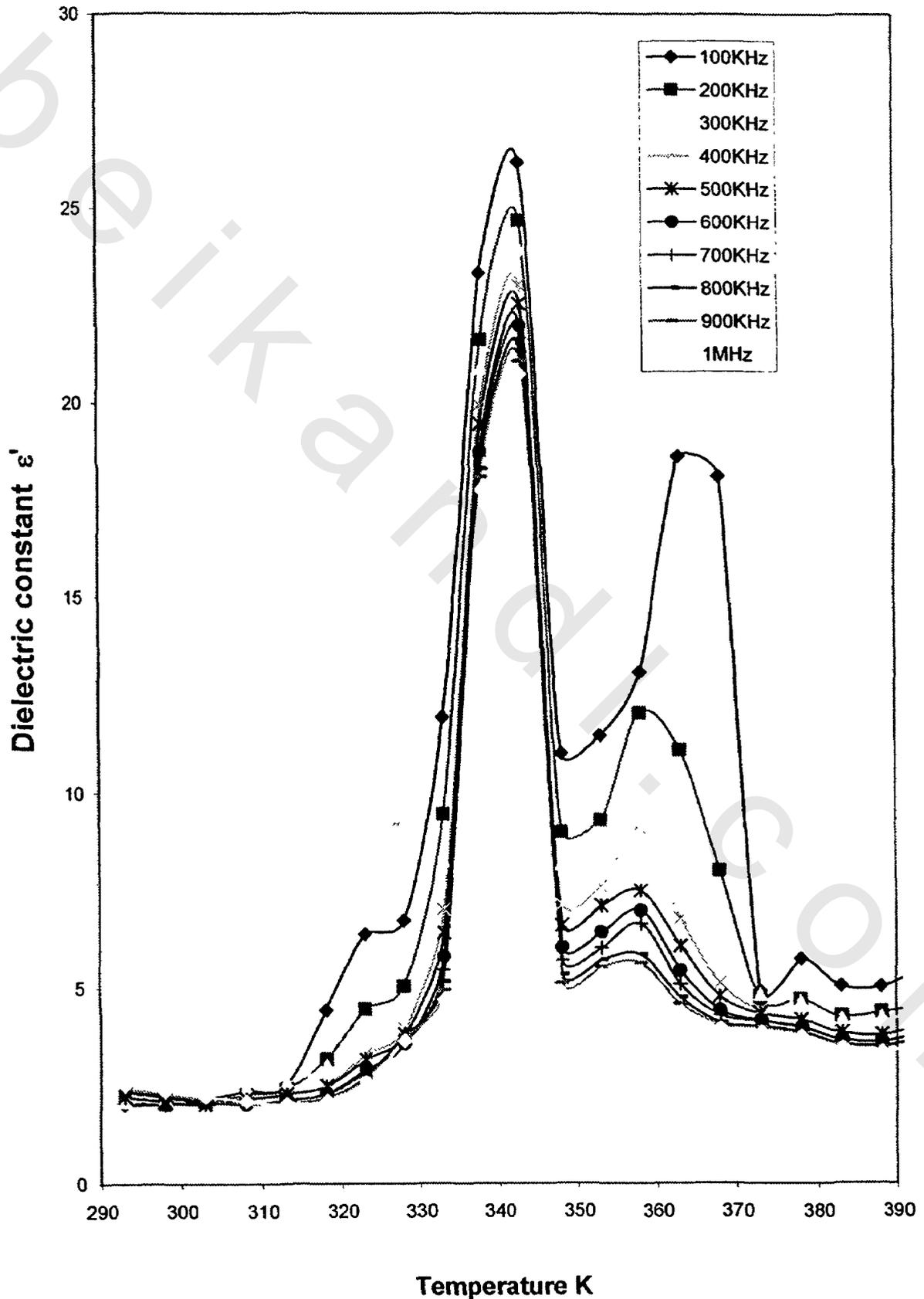


Figure (4.33): Variation of the dielectric constant as a function of temperature at different frequencies for PAA.

4.5.2. The Electrical Permittivity of the Copolymers:

- **In/AN Copolymers:**

The relative permittivity ϵ' for the In/AN copolymers is plotted versus two variable factors, frequency ranging from 100 KHz to 1 MHz and the temperature range from 393 to ≈ 463 K, as shown in figures (4.34) to (4.37). The figures explained that with increasing the temperature, the relative permittivity firstly decreases, until reach certain temperature after which further increasing of the temperature lead to a sharp increase in ϵ' , this is a general behavior for all the samples except the one with 50/50 mol%.

Firstly, due to thermal expansion, the ratio of the number of molecules per unit volume diminishes when the temperature increases, for which reason ϵ' should be, decreased ⁽⁴³⁾.

Secondly the sharp increase in ϵ' is expected to occur above the glass transition temperature, and because of the molecular weight of the copolymer, a certain polymer fraction transforms from a glassy to rubbery state. The glassy-to-rubbery transition enhances the mobility of the polymer segments and facilitates dipole self-organization, which in turns results in an increase in the relative permittivity ⁽⁷¹⁾.

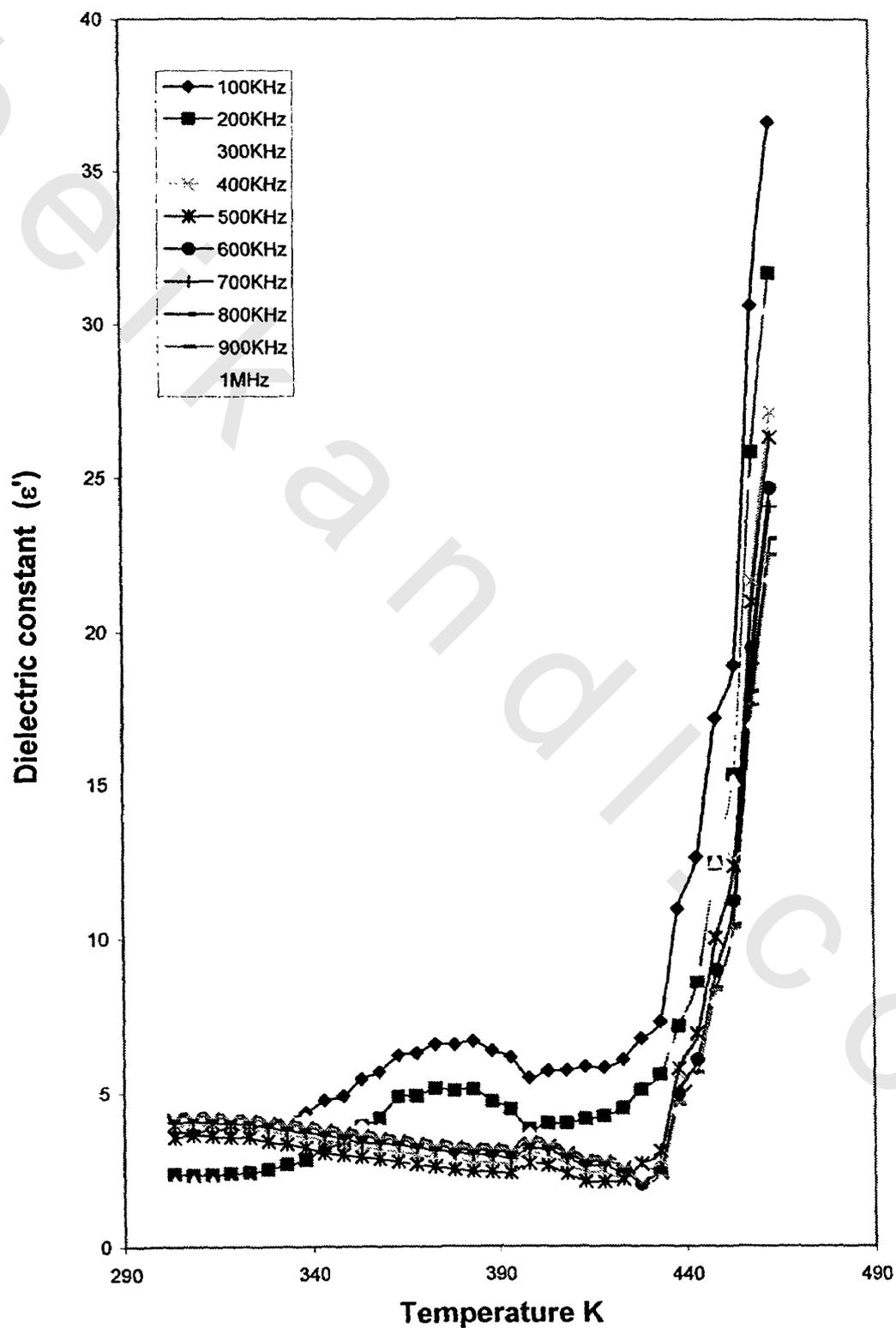


Figure (4.34): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AN of 20/80 mol%.

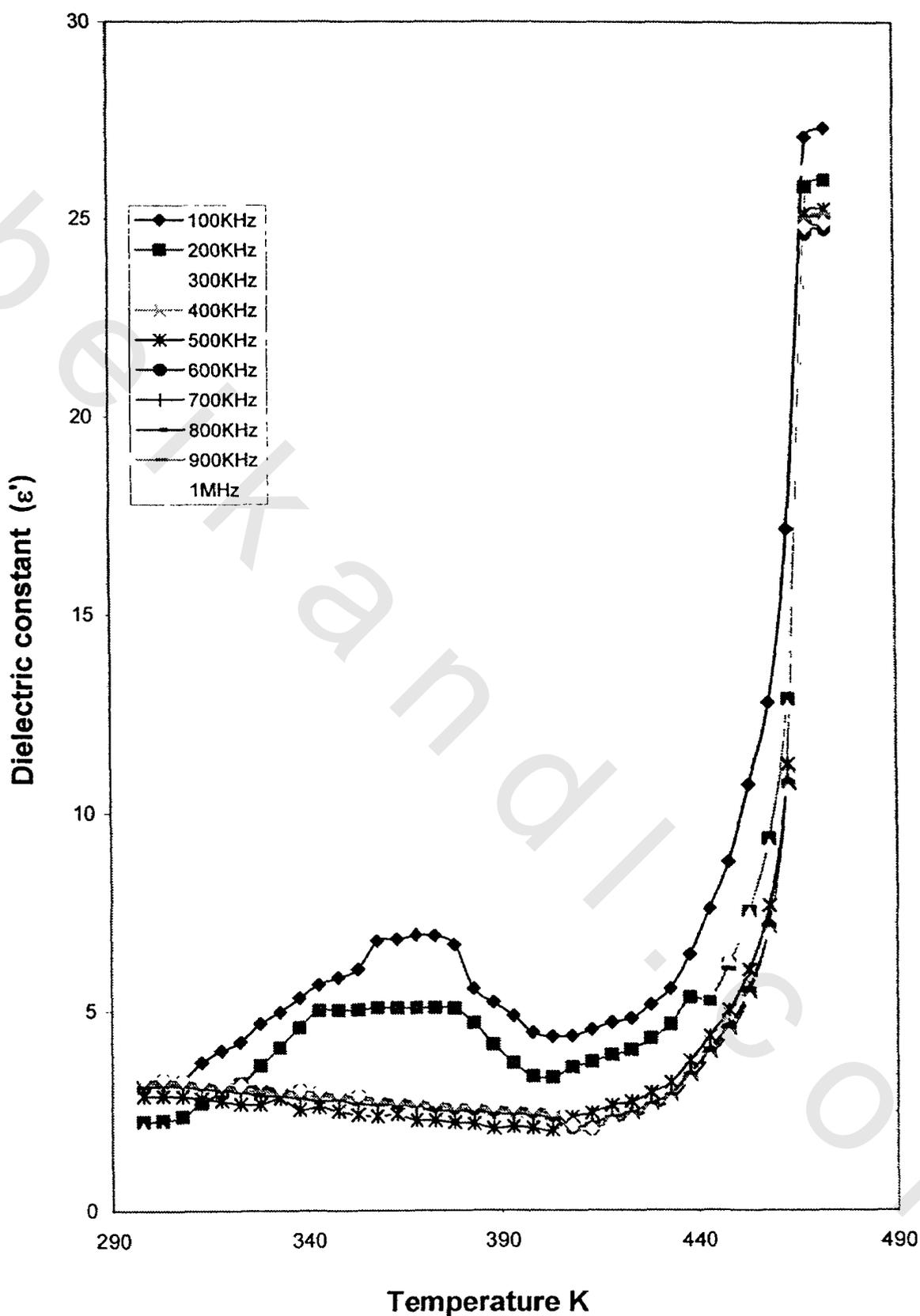


Figure (4.35): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AN of 30/70 mol%.

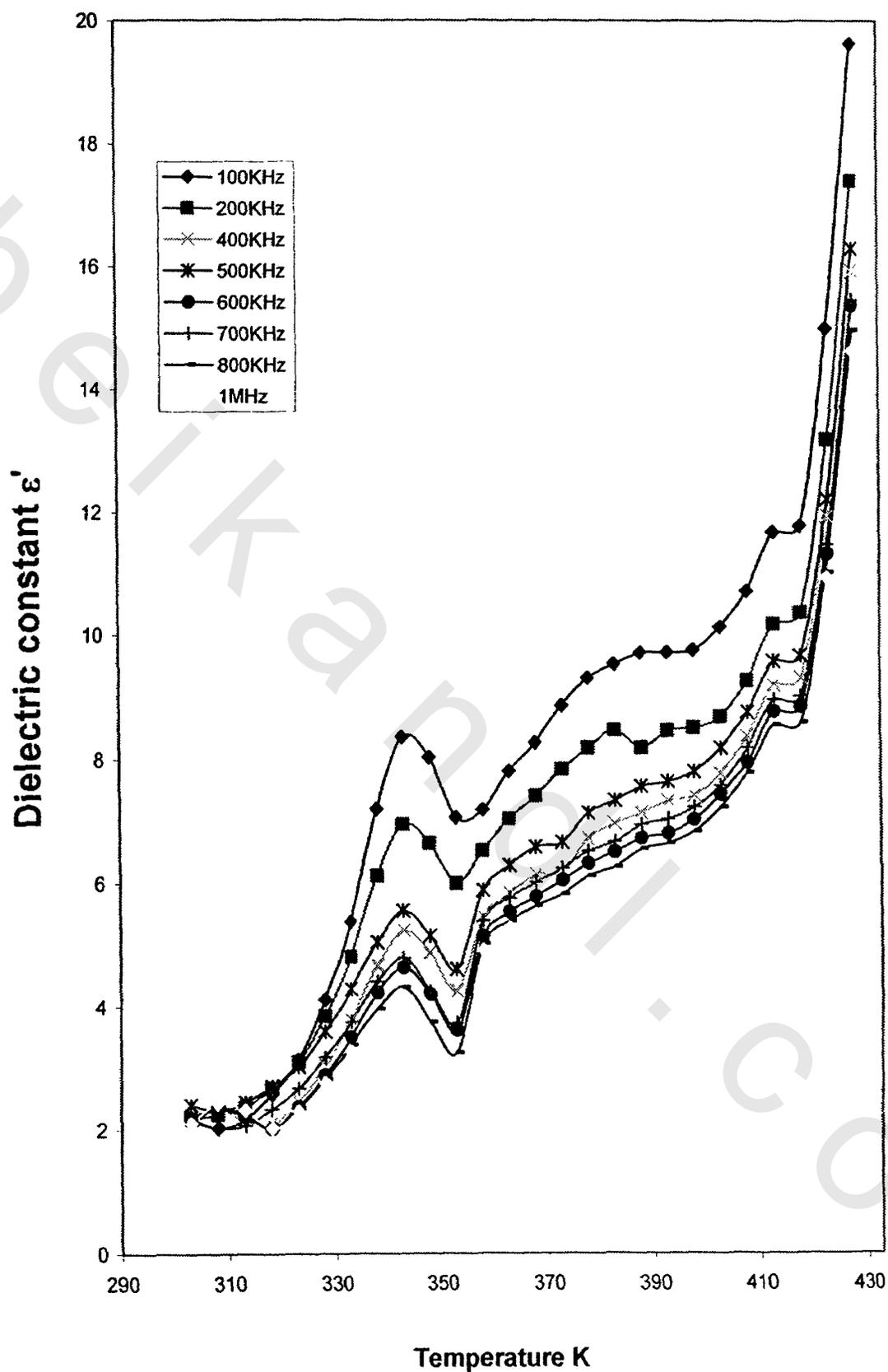


Figure (4.36): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AN of 50/50 mol%.

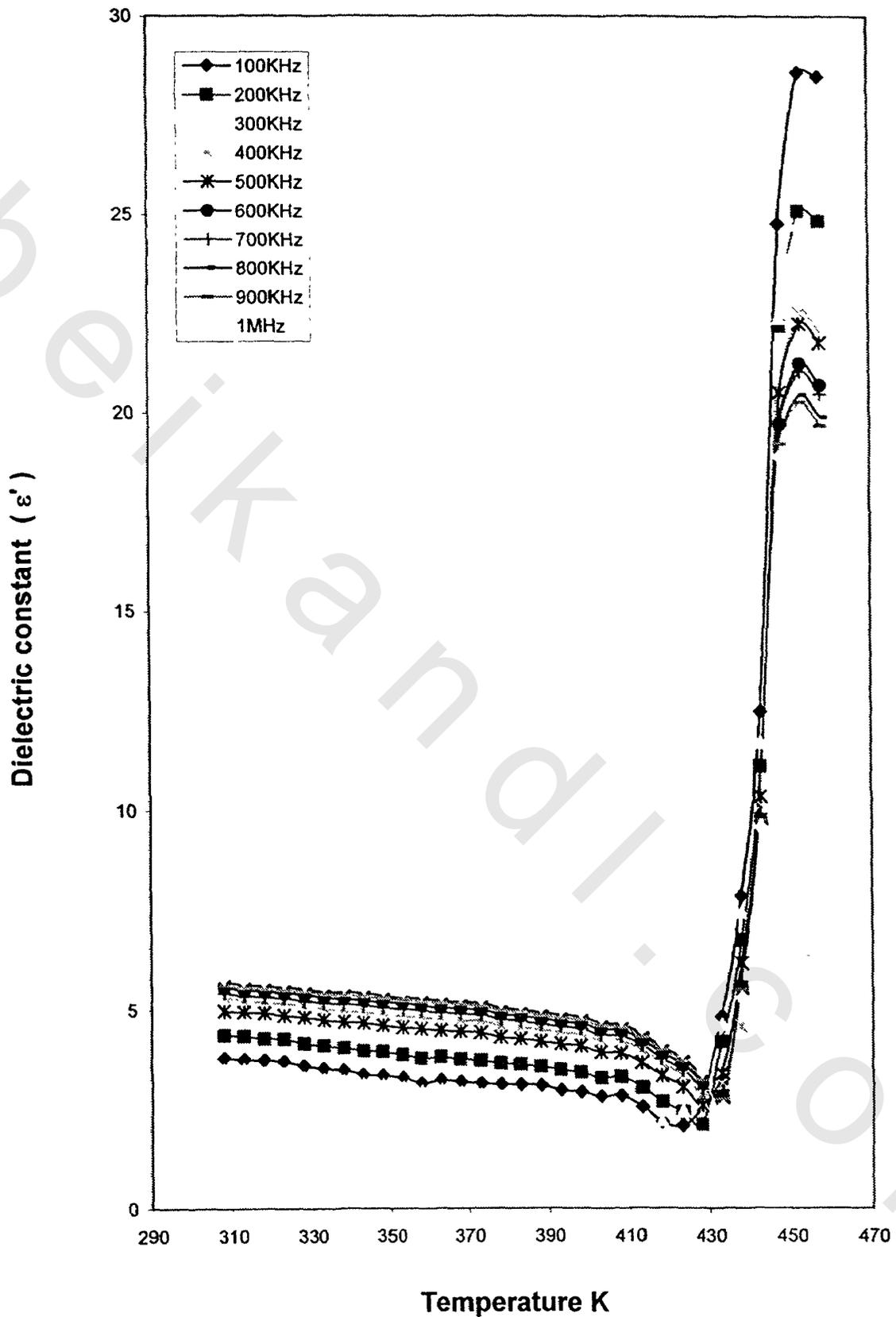


Figure (4.37): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AN of 70/30 mol%.

For sample with the 50/50 mol% ϵ' firstly increases with increasing the temperature until it reaches a small peak after which ϵ' decreases in equivalent temperature then further increasing of temperature leads to a sharp increase in ϵ' . This may be due to the equality of the mol% of the In and AN in the copolymer which makes a stable behaviour like that occurring in PIn or PAN only.

- **In/AA Copolymers:**

The variations of the relative permittivities with the temperature in the frequency range from 100 KHz to 1 MHz for the In/AA copolymers are shown in figures (4.38) to (4.41). It is clear from the figures that the most pronounced feature of the real part of the permittivity ϵ' of the In/AA copolymers are the two peaks which occur at two temperatures t_1 and t_2 as shown in Table (4.16).

Table (4.16): The values of the two temperatures t_1 and t_2 at them the two relaxation peaks of In/AA copolymers occur.

Mol%	20/80	30/70	50/50	70/30
t_1 °K	338	358	373	338
t_2 °K	423	398	398	388

The increase in ϵ' of all the In/AA copolymers with temperature gives two relaxation regions. The existence of these regions may be due to the increase in the mobility of the polymer chains, so the molecular chains with different mobilities try to adjust and align themselves in such a way so as to add to the polarization of the system ⁽⁷²⁾.

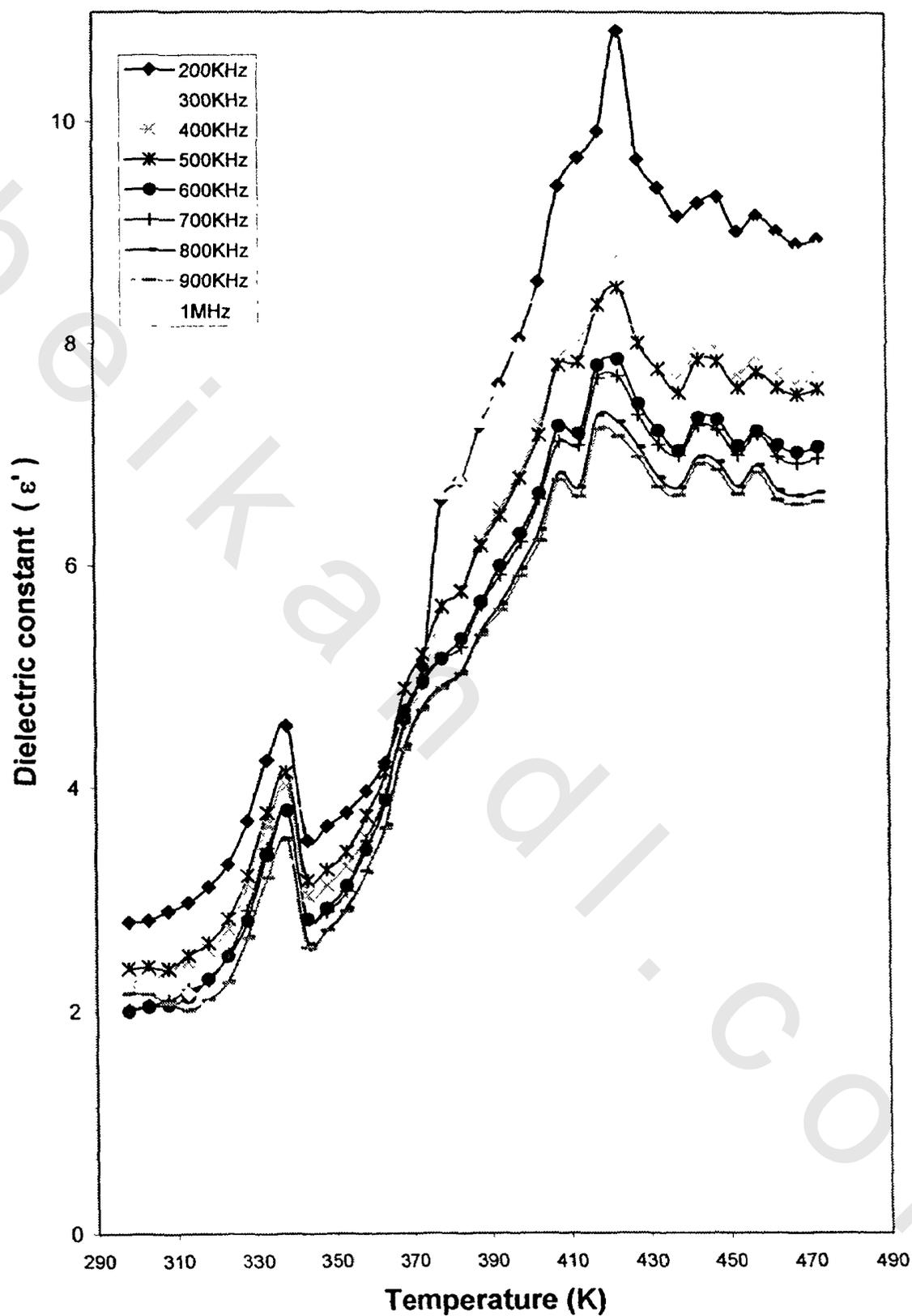


Figure (4.38): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AA of 20/80 mol%.

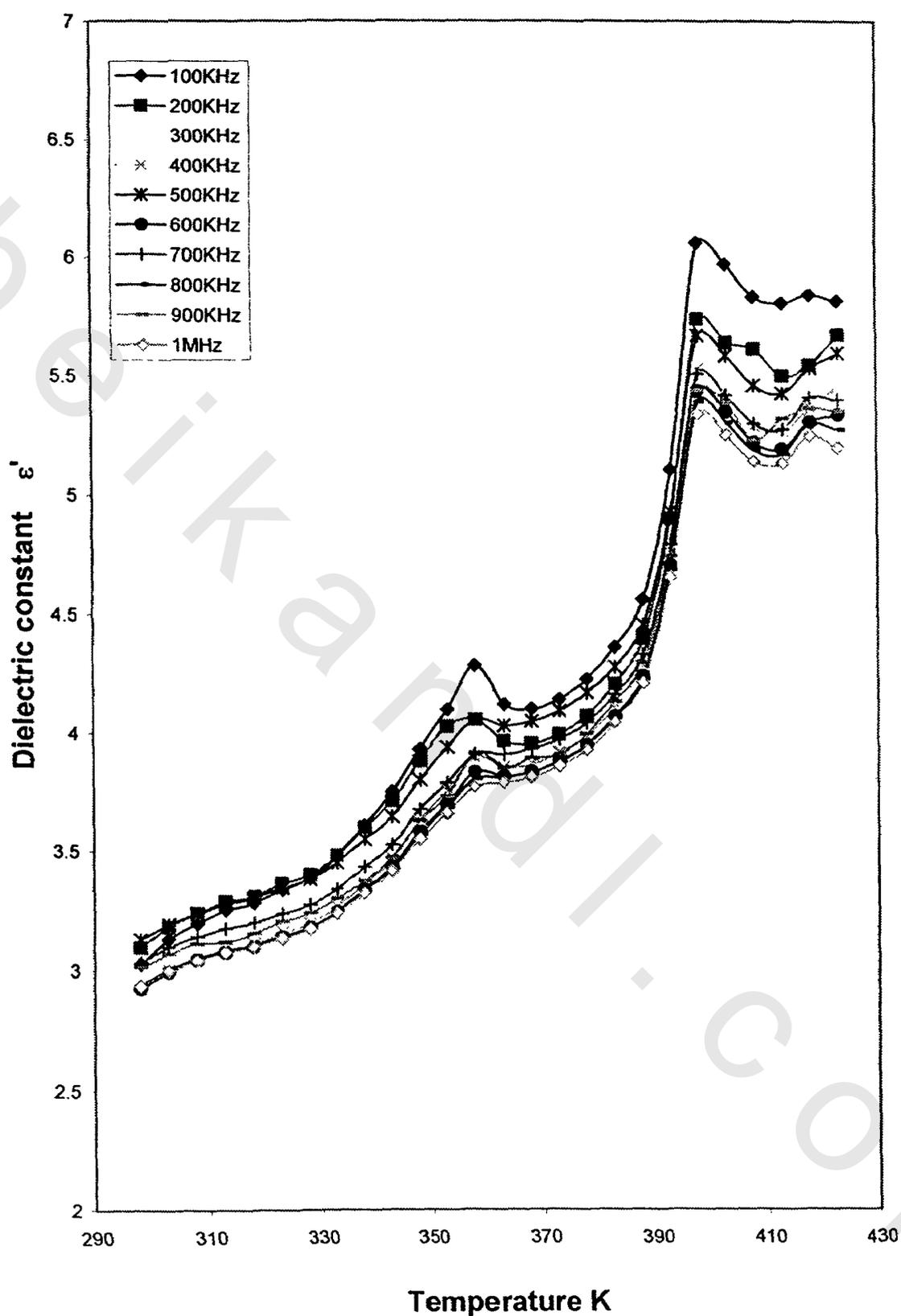


Figure (4.39): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AA of 30/70 mol%.

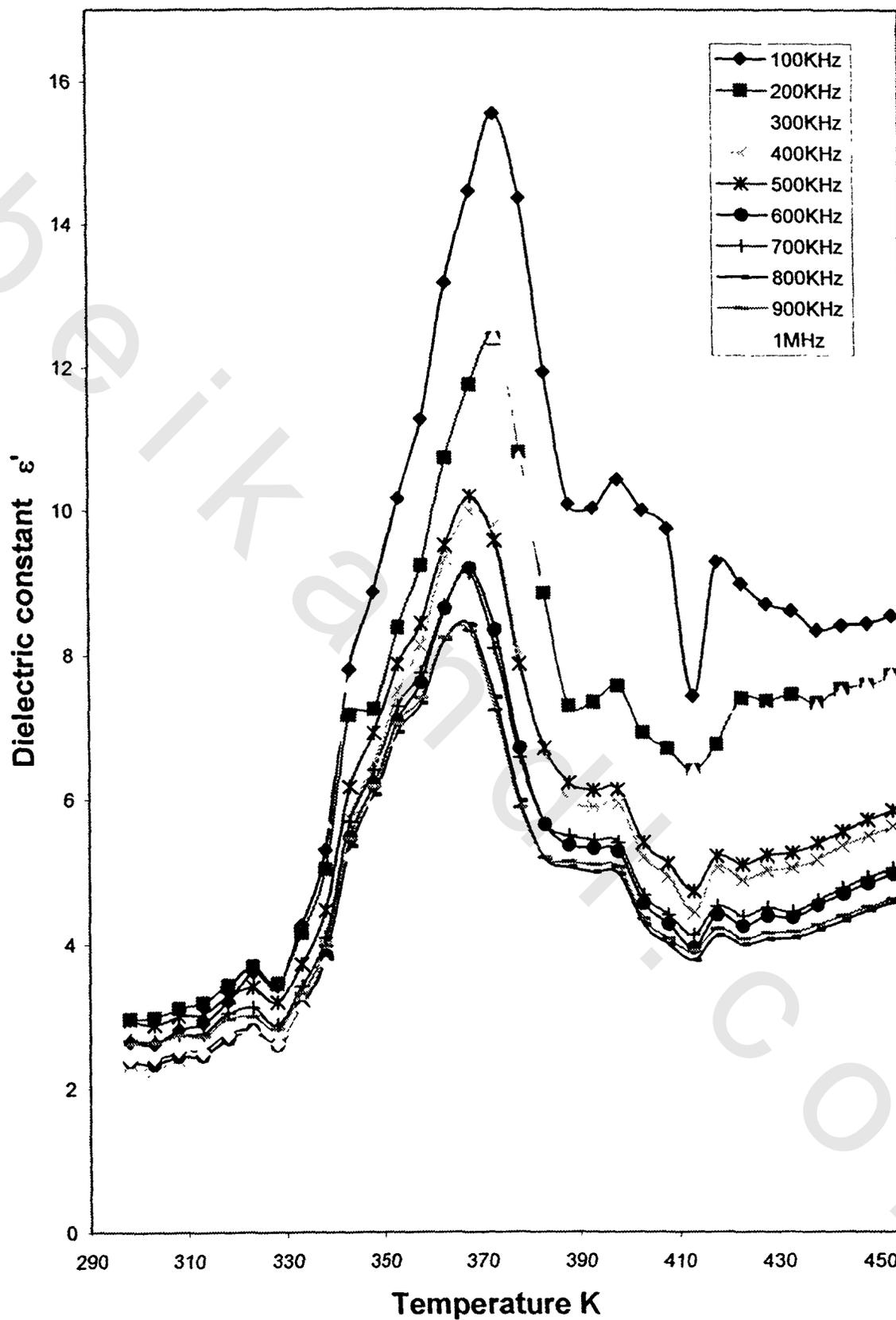


Figure (4.40): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AA of 50/50 mol%.

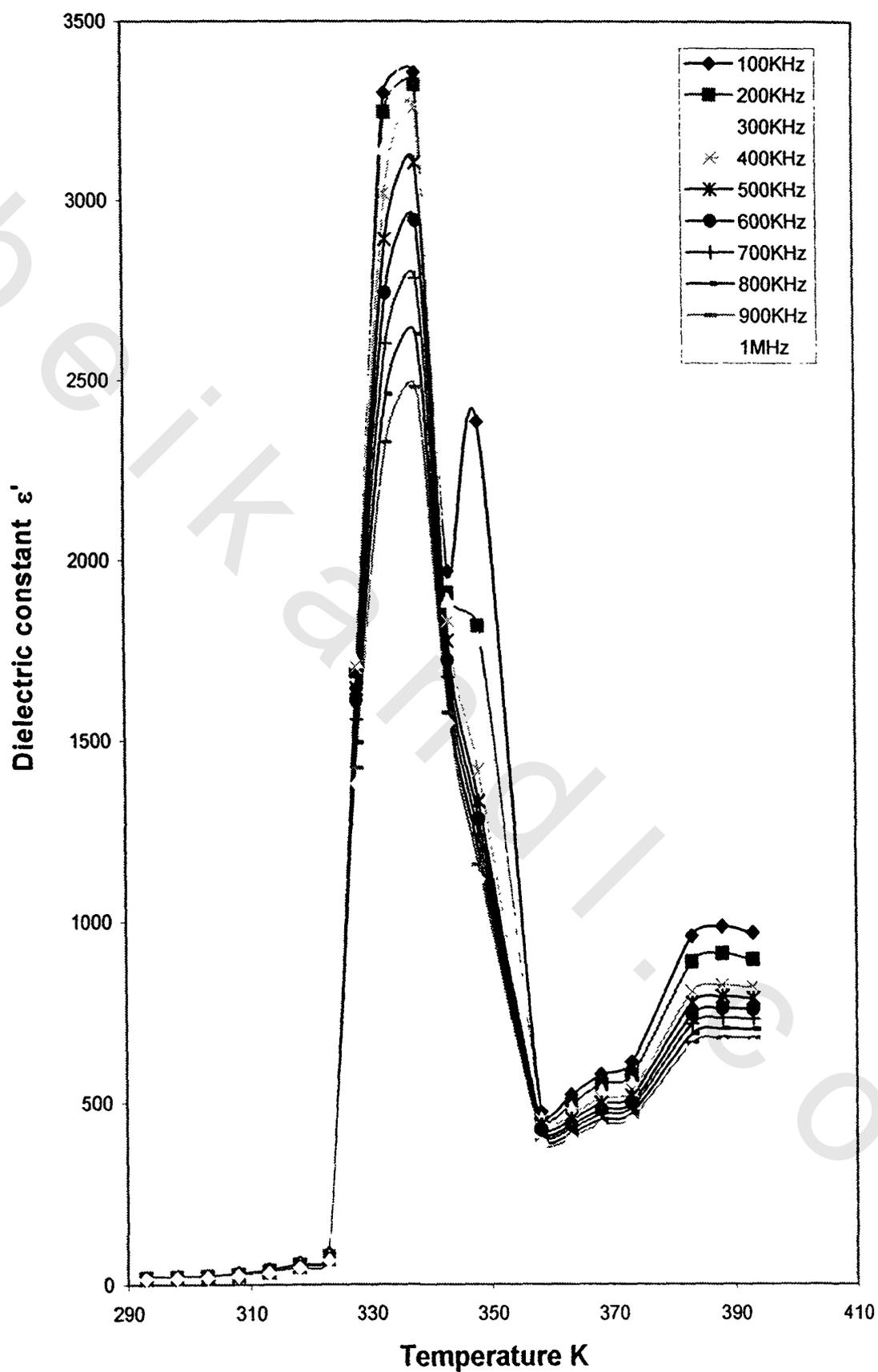


Figure (4.41): Variation of the dielectric constant as a function of temperature at different frequencies for In-co-AA of 70/30 mol%.

4.5.3. The Dielectric Loss Factor of the Homopolymers:

- ϵ'' for Polyindene PIn:

The variations of the dielectric loss factor ϵ'' as a function of the temperature at different frequencies ranged from 100 KHz to 1 MHz for PIn are shown in figure (4.42). From the figure, it is clear that the dielectric loss describes a similar behavior to that of the real part of the relative permittivity, with the existence of two well resolved relaxation peaks.

The maximum values of these relaxations ϵ''_m is dependent on frequency, as by decreasing the frequency ϵ''_m takes higher values, while the temperature at the maximum peak T_m is the same at all frequencies. This can be attributed to the molecular motion arising from the flexible part of the repeating unit which doesn't affect the frequency field ⁽⁷³⁾.

The lower temperature peak designated by β -relaxation at $T_m \approx 328$ K, may be due to the movement of the side groups (Phenyl ring), which are attached to the main chain of the polymer. The higher temperature loss referred to as the α -relaxation and at $T_m \approx 348$ K is attributed to restricted motions of the chain in the polymers with aliphatic sequence ⁽⁷⁴⁾. The figure shows also that each peak has the same shape at all frequencies.

- **ϵ'' for Polyacrylonitrile PAN:**

Figure (4.43) correlates the temperature dependence of the imaginary part of the permittivity ϵ'' for PAN at frequency ranging from 100 KHz to 1 MHz. The curves reveal the existence of more than one relaxation peak. The most prominent one is the maximum peak which arises at temperature about 368 K. This peak is associated with the orientational motion of the CN group. Another relaxation occur at $T_m = 320$ K. This may be due to the combined effect of the high frequency field and increase of the thermal energy which affects the orientational dipoles of the polymer. Also, with increasing the heating temperature up to 390 K one can see another and small peak for high frequencies from 600 KHz to 1 MHz. This peak may be attributed to the additional segments motion faster than those of the two above. The figure investigates also that PAN has the lowest values of ϵ'' where it ranges from 0 to ≈ 16 .

- **ϵ'' for Polyacrylic acid PAA:**

The temperature dependence of the imaginary part of the relative permittivity ϵ'' for PAA at different frequencies ranging from 100 KHz to 1 MHz was measured. Figure (4.44) clears that the dielectric loss describes a similar behavior to that of the real part of the relative permittivity, with the existence of two well resolved relaxation peaks. The high temperature peak occurs at $T_m \approx 363$ K. The low temperature one occurs at $T_m \approx 343$ K.

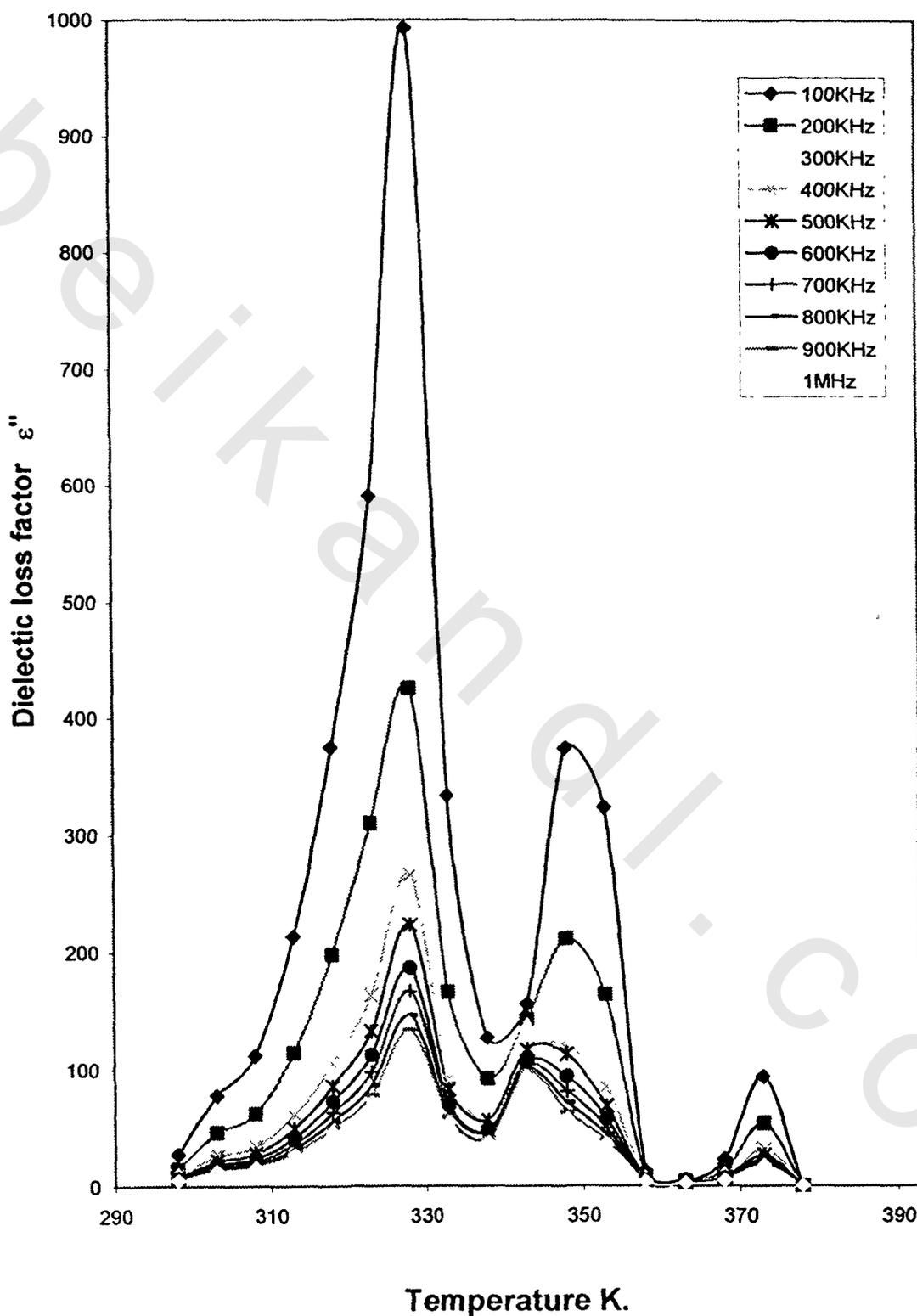


Figure (4.42): Variation of the dielectric loss factor as a function of temperature at different frequencies for Polyindene.

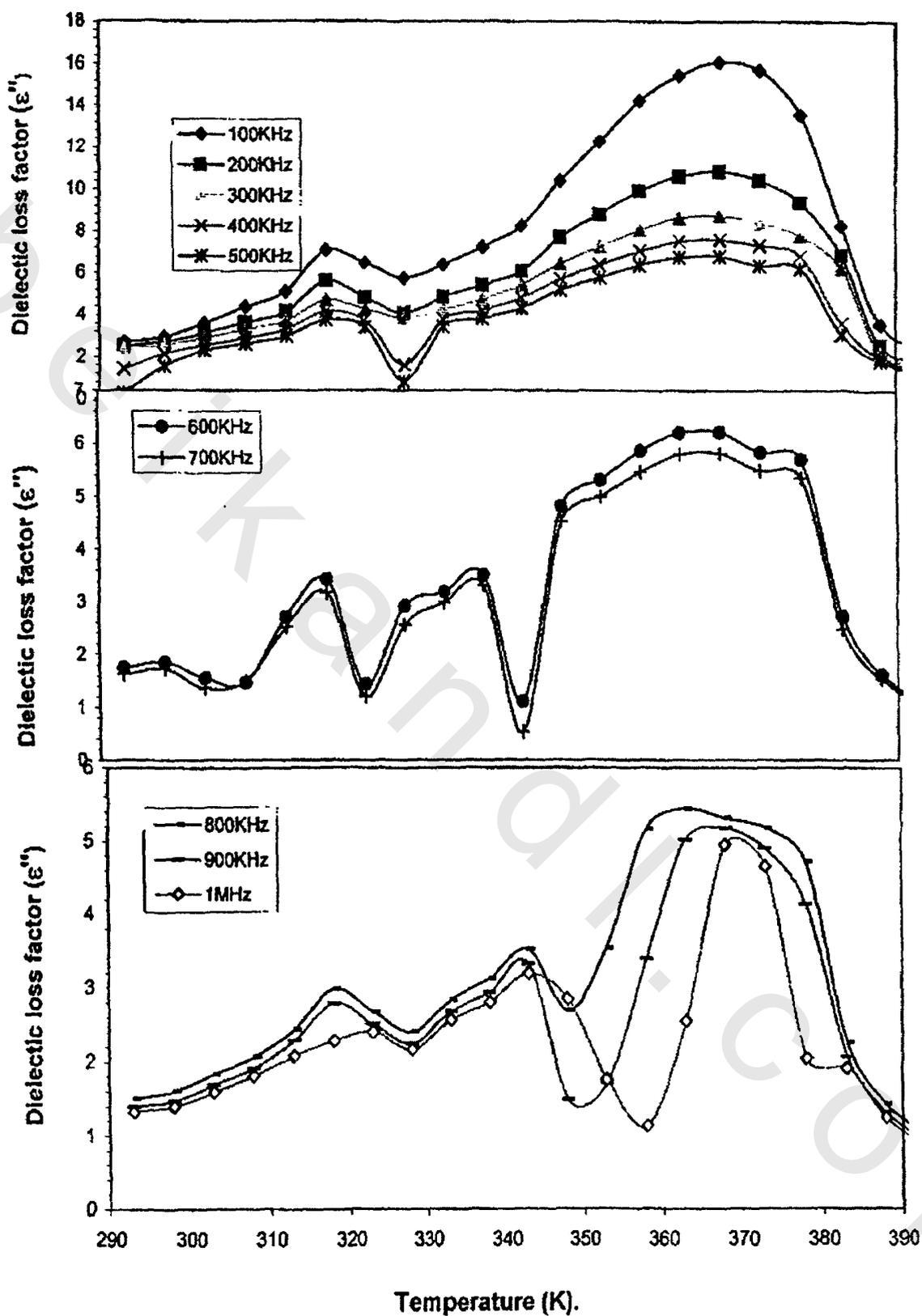


Figure (4.43): Variation of the dielectric loss factor as a function of temperature at different frequencies for Poly AN.

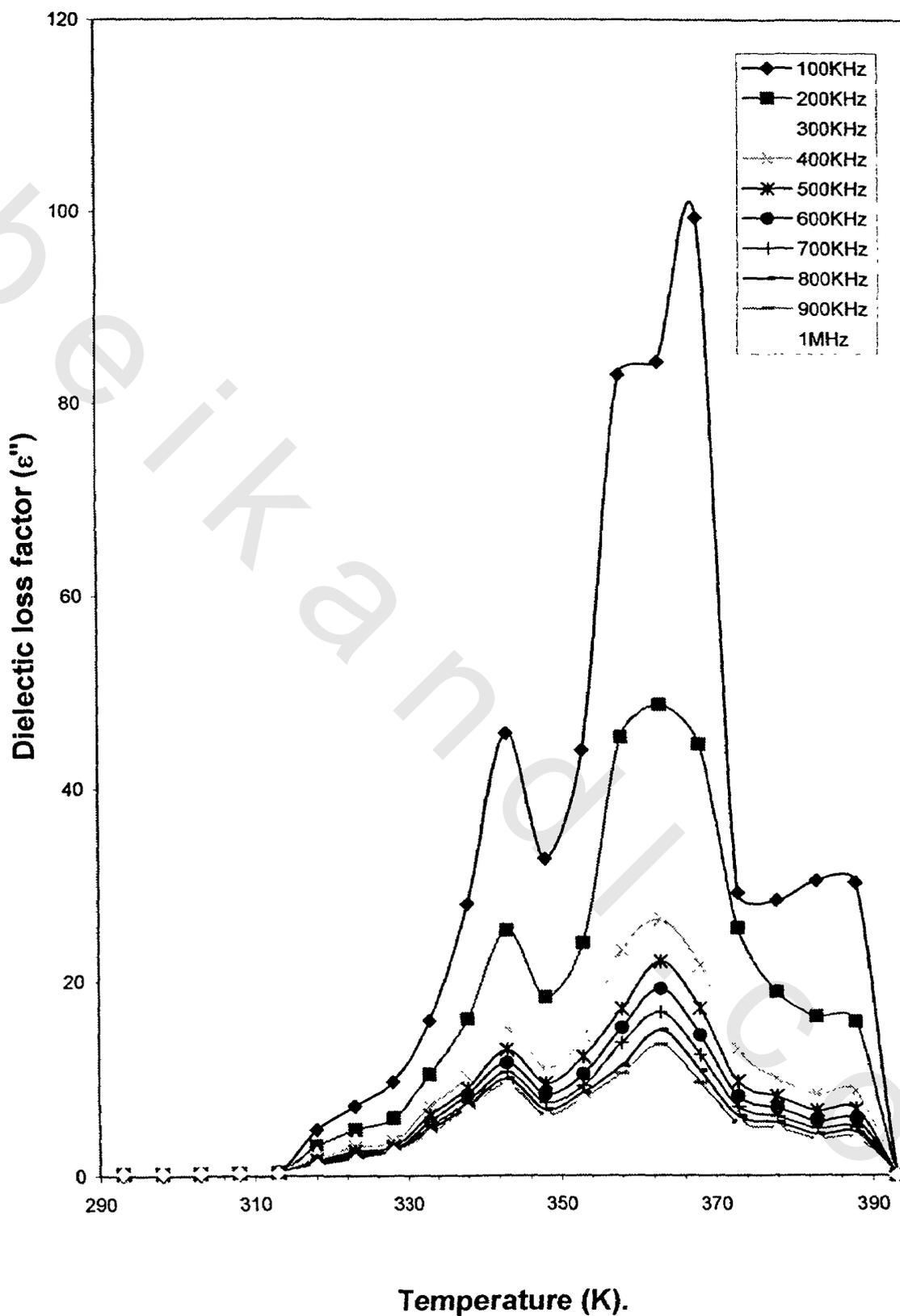


Figure (4.44): Variation of the dielectric loss factor as a function of temperature at different frequencies for Poly AA.

The dielectric relaxation arising from the molecular motion in the crystalline region in polar polymers are generally attributed to the rotation of the dipoles due to chain rotation or twisting around the molecular axis ⁽⁷⁵⁾. A relaxation may be related to the coupled motion of the chain folds and the interior parts of the lamellar crystals ⁽⁷⁶⁾. The figure indicates also that each peak has the same shape at all frequencies. The value of ϵ'' of PAA is ranging from 0 to 100.

4.2.4. The Dielectricloss Factor of the Copolymers:

- **In/AN Copolymers:**

The dielectric loss factor ϵ'' plotted versus temperature at different frequencies ranging from 100 KHz to 1 MHz In/AN copolymers with different mol % of the copolymer composition is shown in figures (4.45) to (4.48).

The most prominent feature of the curves is the existence of only one relaxation (labeled α relaxation) for all the samples except one sample with 50/50 mol % of In/AN for which ϵ'' has two relaxation peaks. A sudden increase of ϵ'' is observed in all the samples, such an increase is frequently associated with the second relaxation process. The nearly flatness observed in the α -relaxations may be due to the combined effect of high frequency and high thermal energy.

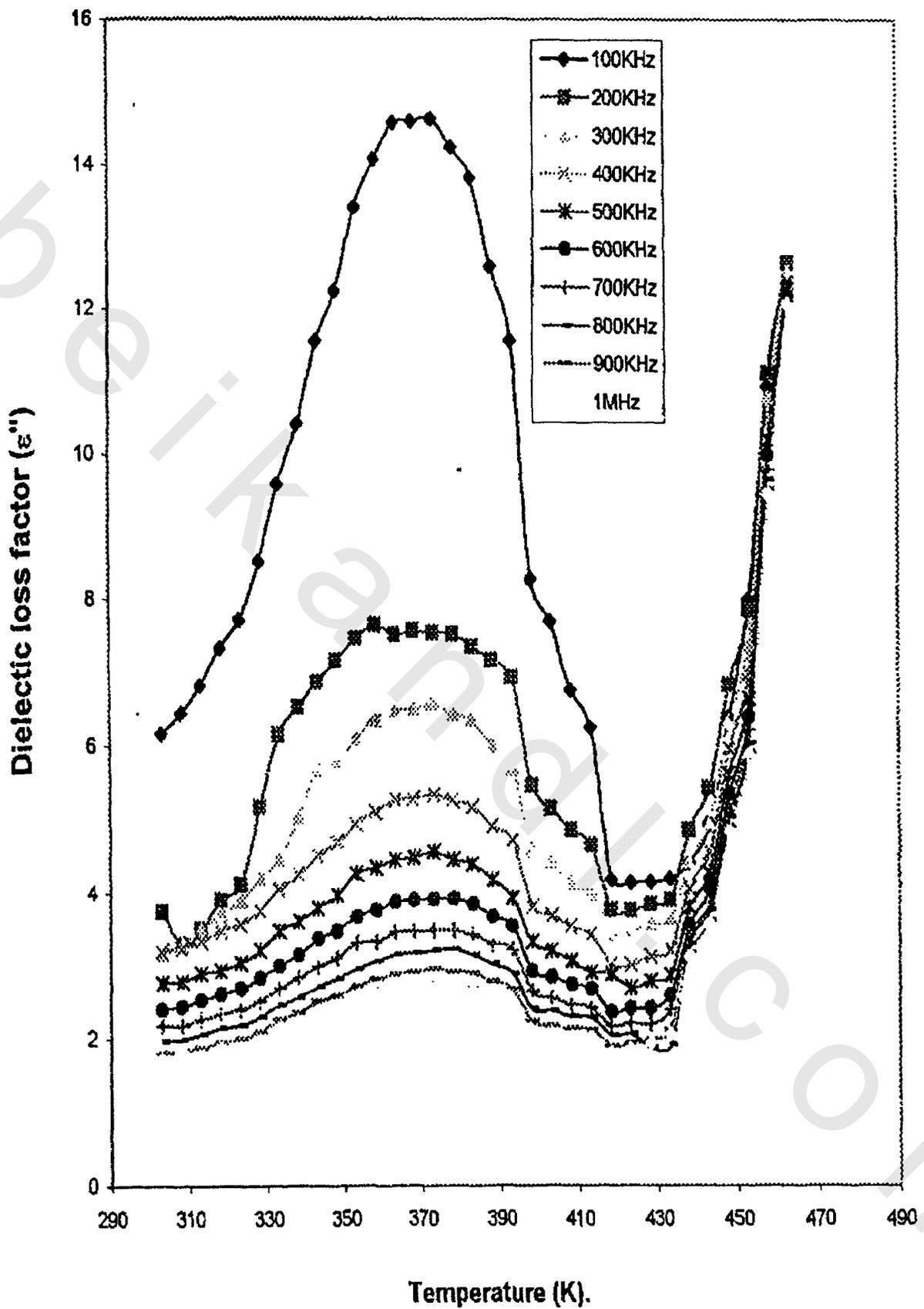


Figure (4.45): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AN of 20/80 mol%.

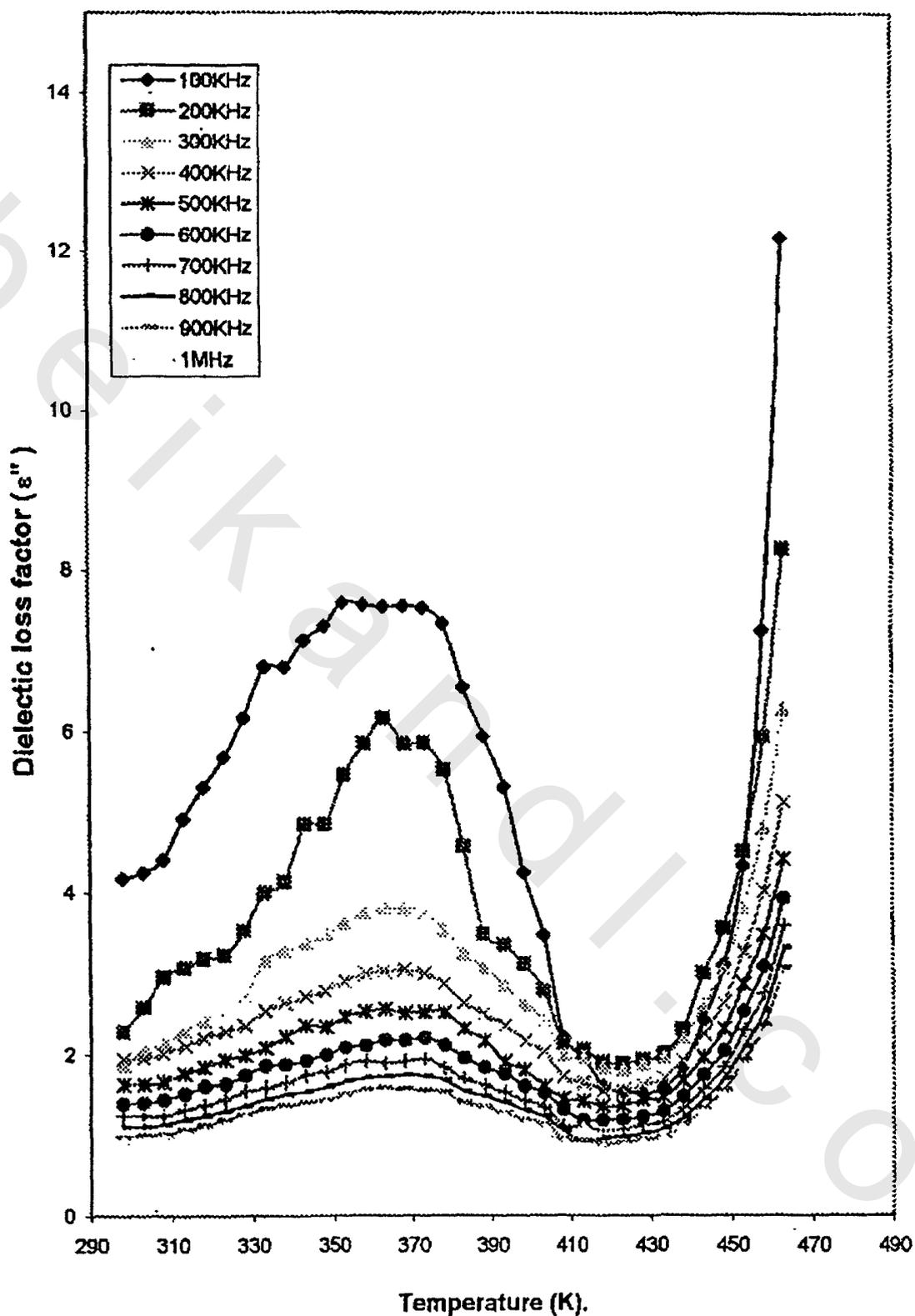


Figure (4.46): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AN of 30/70 mol%.

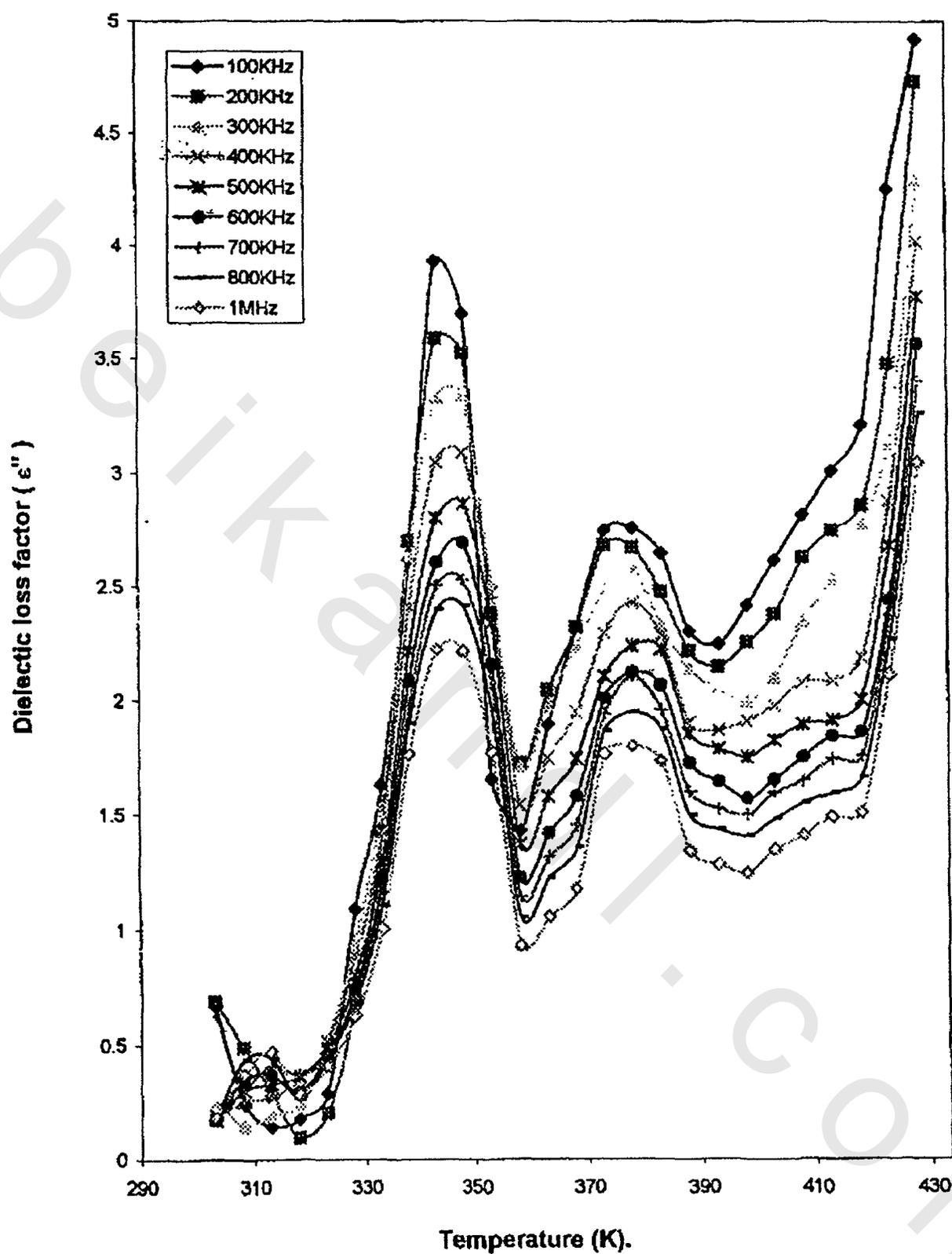


Figure (4.47): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AN of 50/50 mol%.

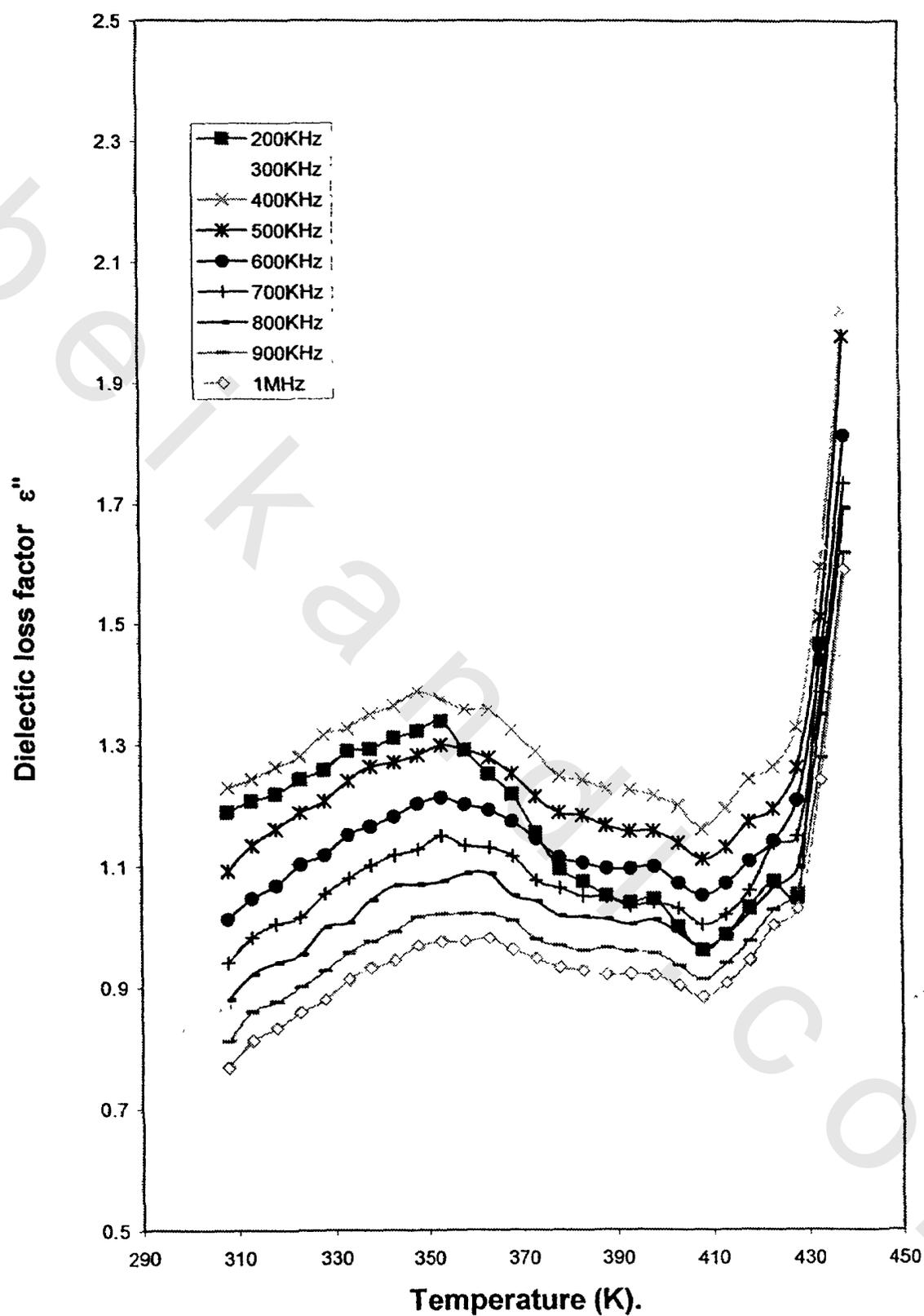


Figure (4.48): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AN of 70/30 mol%.

The copolymer composition of the In/AN equal to 50/50 mol% shows two relaxation peaks; the higher temperature peak is called α -relaxation which is attributed to motion of chain back bone of the copolymer. The second peak labeled β relaxation in the low temperature side. This may be attributed to the movement of the side groups.

- **In/AA Copolymers:**

The variation of the dielectric loss factor ϵ'' of the In/AA copolymers as a function of the temperature at different frequencies ranged from 100 KHz to 1 MHz are shown in figures (4.50) to (4.53). In all the samples, two main relaxation regions were detected which have been labeled as α and β , except one sample of 20/80 mol% which show three relaxation regions. The location and the strength of these relaxations were observed from the figures. Both ϵ''_m and T_m are different for each polymer. The values of ϵ''_m are dependent on the frequency, as with decreasing the frequency, ϵ''_m is increased. But the value of T_m for each peak is approximately the same at all frequencies for all the copolymers. The figures show that the value ϵ''_m decreases as the mol% of indene in the copolymer increases.

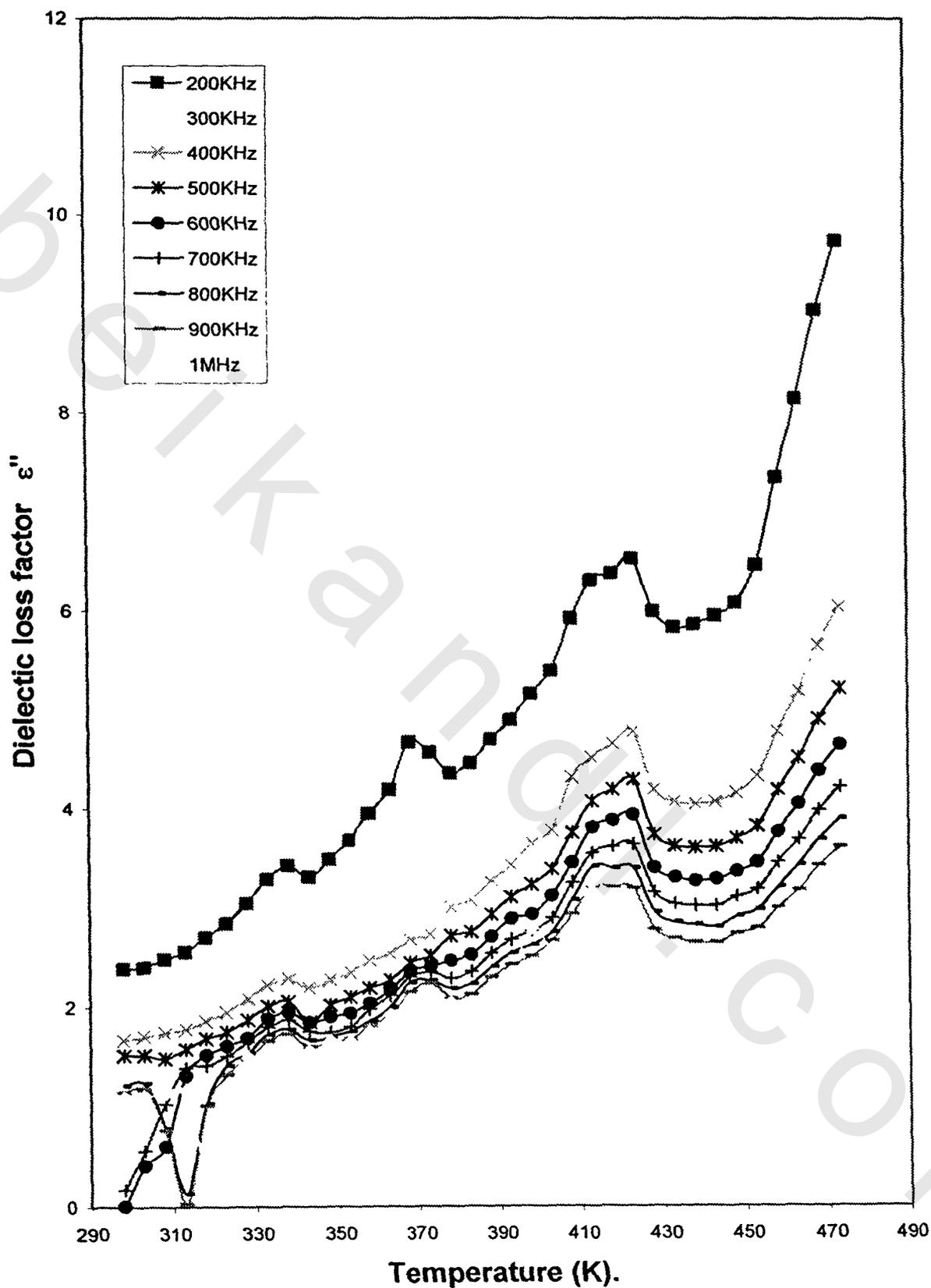


Figure (4.49): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AA of 20/80 mol%.

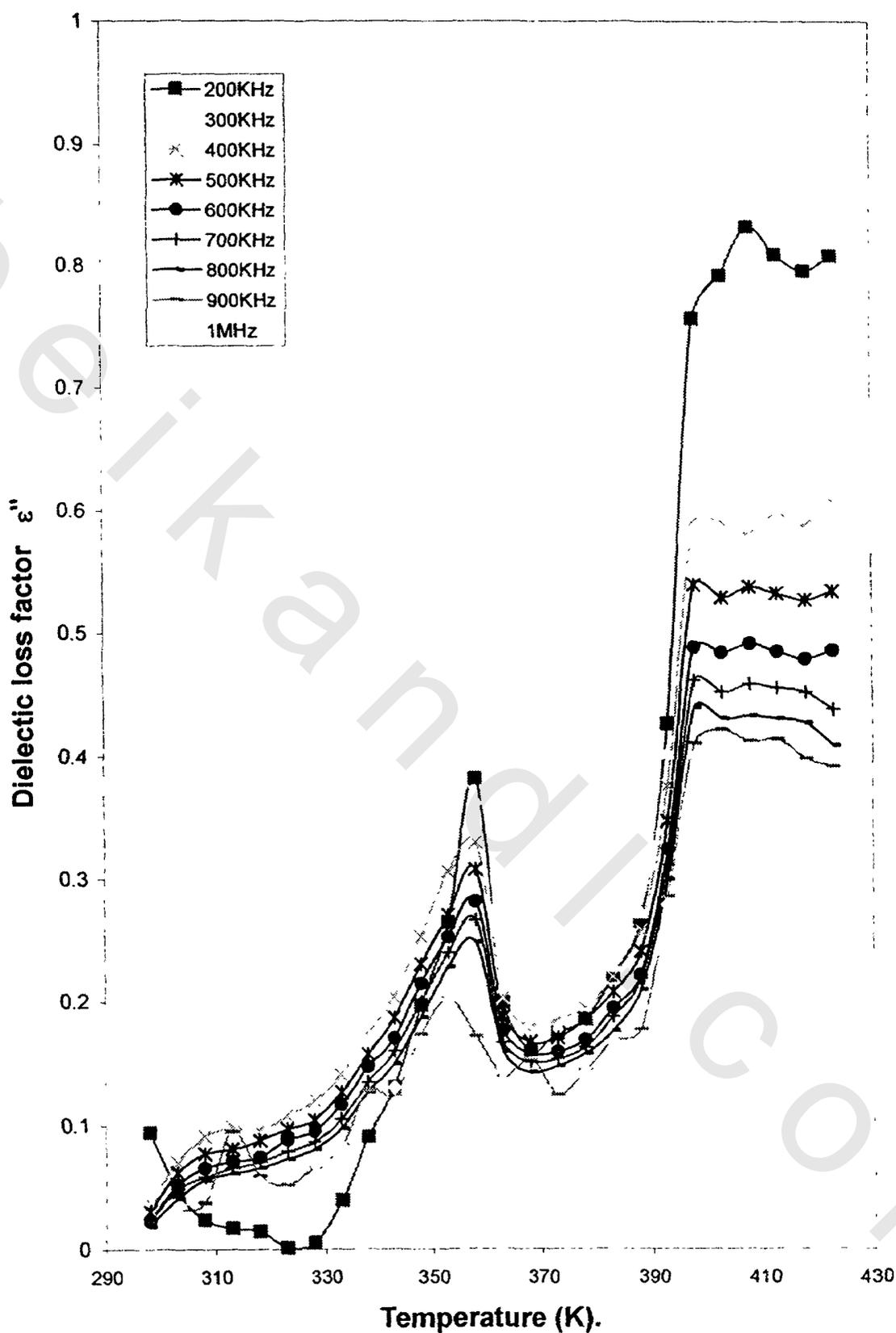


Figure (4.51): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AA of 30/70 mol%.

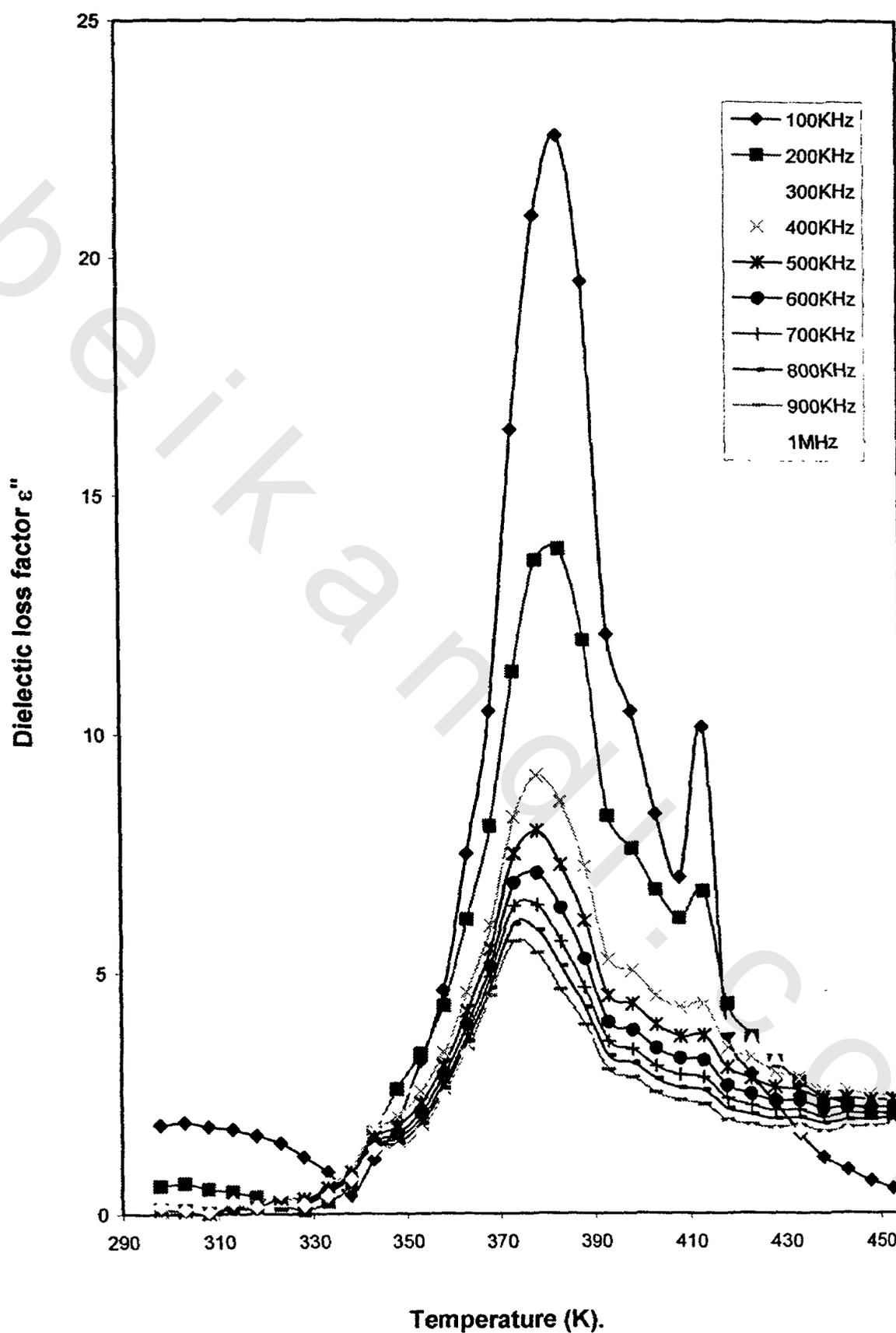


Figure (4.52): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AN of 50/50 mol%.

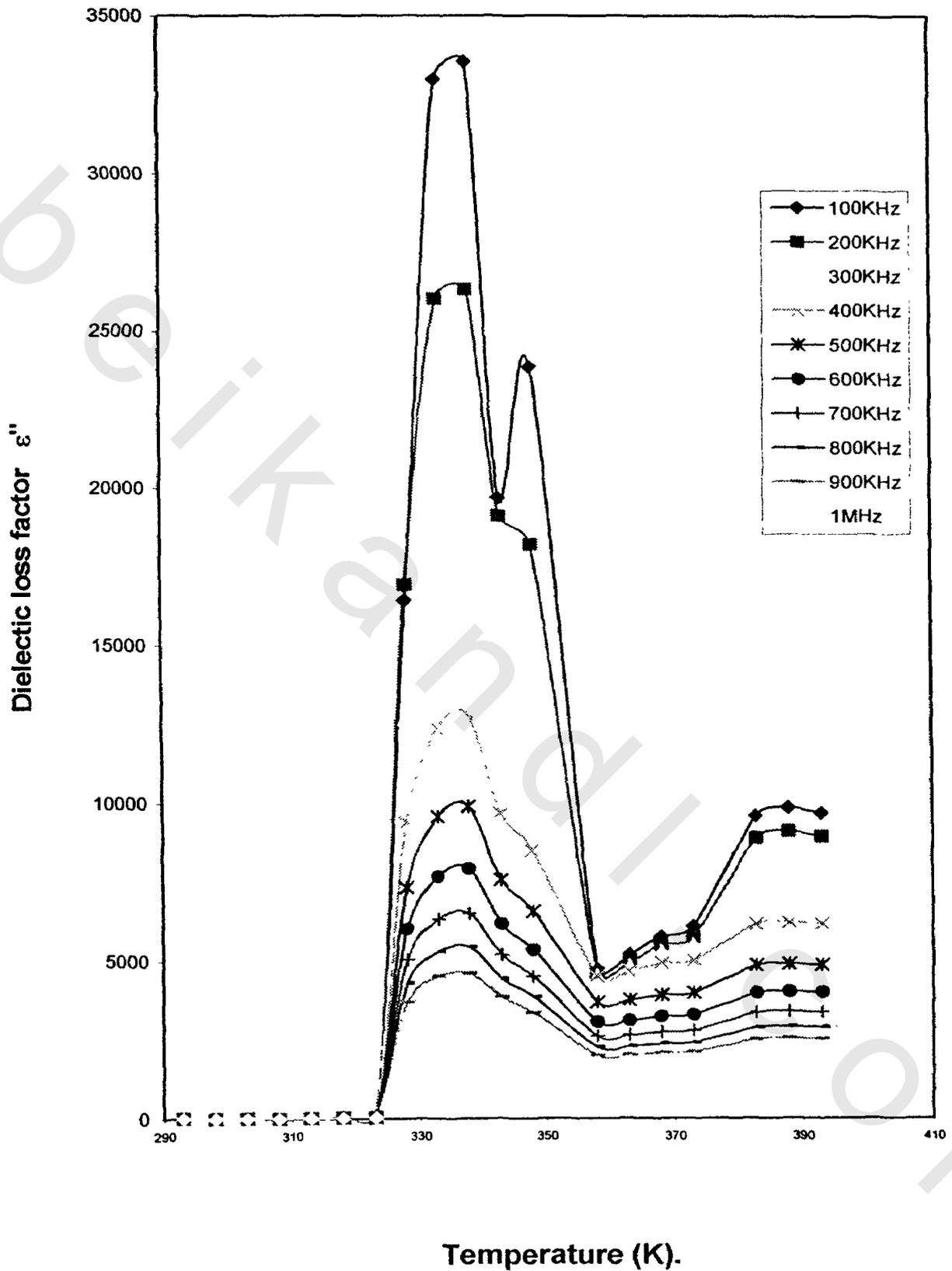


Figure (4.53): Variation of the dielectric loss factor as a function of temperature at different frequencies for In-co-AA of 70/30 mol%.