

Dynamic Mechanical Analysis of Poly(trimethylene terephthalate)—A Comparison with Poly(ethylene terephthalate) and Poly(ethylene naphthalate)

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ABSTRACT: The fiber properties of PTT have been the subject of several reports, although very few reports describe the properties of molded specimens. In this work, the dynamic mechanical relaxation behavior of compression-molded PTT films has been investigated. The added flexibility of the PTT was found to lower the temperature of the β - and α -transitions relative to the PET and PEN. The results suggest that the β -transition is at least two relaxations for PET and PTT due to the increase in the breadth of the relaxation. The results seem to support the hypothesized

mechanism of others, in that the β -transition involves the relaxation of the carbonyl entity and the aromatic C1–C4 ring flips for PTT and PET, and the relaxation of the carbonyl for PEN. The β^* - and α -transitions for all three polymers seem to be cooperative in nature. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2791–2796, 2004

Key words: relaxation; activation energy; transitions; polyesters

INTRODUCTION

Poly(trimethylene terephthalate), PTT, has recently been commercialized by Shell for both fiber and injection-molding applications¹ following the development of new process offering the production of 1,3-propanediol at a much lower cost.² The fiber properties of PTT have been the subject of several reports,^{3–6} whereas very few reports describe the properties of molded specimens.^{1,7} It is the intention of this work to investigate the dynamic mechanical relaxation behavior of compression molded PTT films, for although much is known about the relaxations in poly(ethylene terephthalate), PET and poly(ethylene naphthalate), PEN, much less is known about PTT. Indeed, there is a considerable quantity of literature available on the mechanical relaxations of PET and PEN,^{8–16} and although the molecular origins of these processes have been subject to some debate, there is a growing consensus as to the molecular motions contributing to the α - and β -transitions. The chemical structures of all three polymers are shown in Figure 1.

It has been shown by English⁸ in a series of NMR experiments that the molecular motions in the polymer chain below the α -relaxation are attributed to the phenyl ring flips. English⁸ examined selectively deuterated PET and identified significant motion of the

ethylene glycol units at the glass transition, attributed to the *trans-gauche* motion. At lower temperatures, however, a second relaxation process was identified that appeared to be consistent with the β -relaxation. The β -relaxation process has a considerably lower activation energy than the glass transition process, and is attributed to the motion of the phenyl rings. Interestingly, it appears that the ethylene glycol units do not contribute significantly to the relaxation processes present in the β -relaxation region. Later work has subsequently confirmed the importance of phenyl ring flips in PET below the glass transition.^{8–16} For example, work conducted by Maxwell et al.⁹ using ¹³C and deuterium NMR on the effect of low molecular mass additives on the secondary relaxation process in PET led them to conclude that there is a significant increase in the molecular mobility of the phenyl rings at temperatures and frequencies consistent with that of the β -relaxation process. In addition, like English,⁸ they found that the phenyl rings undergo 180° ring flips during the β -relaxation, and that there is relatively little molecular mobility of the ethylene glycol groups in PET, below the glass transition temperature.

In subsequent work, Maxwell et al.¹⁰ also compared dielectric spectroscopy results with the previous findings and observed that the two tail ends of the β -relaxation peak are associated with different molecular motions. The high temperature end of the β -relaxation peak is associated with the motion of the C1–C4 phenyl ring flips and is more sensitive to the addition of additives. The low-temperature end of the β -relax-

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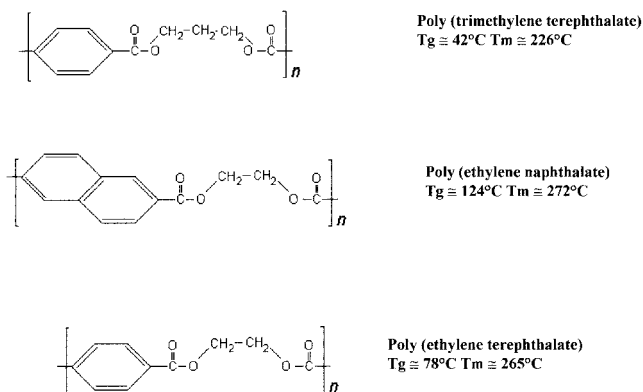


Figure 1 Chemical structure of PTT, PEN, and PET.

ation peak is related to the relaxation of the carbonyl group and is less affected by additives.

Menegotto et al.¹¹ used a combination of thermally stimulated current measurements, TSC, and dielectric spectroscopy to investigate the β -relaxation peak for PET. The β -relaxation peak was described in terms of a distribution of relaxation times. At lower frequency, the TSC technique revealed two components in the β -relaxation process. The temperature of the distribution of relaxation times were analyzed from both dielectric techniques. Whereas the maximum and lower time component of the relaxation time distribution extracted by TSC was stated to be associated with the noncooperative motion of the carbonyl groups, the upper time component extracted by dielectric spectroscopy was assigned to the cooperative phenyl ring flips.

Abis et al.^{12,13} investigated the dynamics of amorphous aromatic polyesters consisting of PET, PEI, and PEN by means of solid-state ¹³C NMR. The study attempted to gain a direct comparison of molecular motion of the solid copolyesters, as it is believed that this would gain a useful insight regarding their different macroscopic properties, especially with respect to their gas barrier properties. The study found that for PEN and PEI the relaxation parameters were similar, while for PET, a higher fraction of mobile domains is constantly found, especially for the aromatics.

Investigation of PET-PEN copolymers has proven most useful in elucidating the molecular motions occurring in the relaxation process. McGonigle et al.¹⁵ investigated a series of PETN copolymers and found that the activation energy of the β -relaxation for all copolymers studied changed very little, indicating that the dipole relaxation process has a common origin and can be ascribed to motion of the linking polar entity. Most recently in a study by Hardy et al.,¹⁶ the relaxation behavior of PEN was studied by dielectric spectroscopy and dynamic mechanical measurement. Both methods of analysis showed three relaxation pro-

cesses occurring. In order of descending temperature they are the α -relaxation due to the glass transition, second, the β^* process due to the cooperative motion of the naphthalene groups, and finally, the β -relaxation process, which is assigned to the local molecular motions of the carbonyl group.

To date, very little work has been published on the mechanical relaxations in PTT. Ward et al.¹⁷ conducted dynamic mechanical measurements on a series of alkylene terephthalate polymers where the methylene sequence was varied from $n = 2$ (as in PET) to $n = 10$.¹⁷ With increasing numbers of methylene groups the two main loss peaks moved by equal amounts to lower temperatures. For $n = 10$, the β peak at 100 Hz was at -125°C , very close to the γ transition in polyethylene. This was thought to add weight to the previous explanation by Thomson and Wood, who, in 1956, remarked that the β transition was associated with the motions of the aliphatic segment of the chain.¹⁸ However, broadline NMR has shown these polymers and deuterated derivatives to possess only very small molecular motions occurring over the temperature range of these transitions.

Farrow et al.¹⁹ stated that the β -relaxation contained at least two superimposed loss processes due to asymmetry of the loss peak, which reversed as the methylene sequence length increased, even showing a distinct shoulder at $n = 9$; on this basis Farrow stated that these motions could be associated with the restricted motion of the ethylene glycol residue. Illers and Breuer²⁰ gave an alternative explanation of peak asymmetry, after a detailed examination of the relaxation process, by stating the loss peak involved a total of three relaxations the first at -165°C , which was stated to involve the hindered rotation of the CH₂ groups. They attributed the other two peaks at -105 and -70°C to the motions of the *gauche* and *trans* conformations, respectively, of the ethylene glycol moiety.²⁰ However, in view of the work of Ward and others,⁸⁻¹⁶ this does not seem to be the case.

EXPERIMENTAL

Materials

PET (Laser+[®]) and PEN were supplied by DuPont Polyester, Wilton, UK, in the form of extruded sheet. PTT came in the form of extruded granules, supplied by Shell Chemical, Louvain-la-Neuve, Belgium. Properties of materials are given in Table I.

To give the samples the same thermal history, all samples were compression molded in a Moore press at 290°C and were quenched directly into liquid nitrogen. To limit hydrolysis in the melt state during molding, all sample were predried in an air oven at 140°C for 24 h.

TABLE I
Molecular Masses, Glass Transition Temperatures, and Intrinsic Viscosities of the Melt Cast Amorphous Sheets

	T_g by DSC/°C	$M_w/g \text{ mol}^{-1}$	$M_n/g \text{ mol}^{-1}$	M_w/M_n	IV/dl g^{-1}
PTT	42	35,200 ^b	17,300 ^b	2.03	0.92 ^b
PET	78	106,000 ^a	37,400 ^a	2.85	0.81 ^a
PEN	124	69,300 ^a	28,700 ^a	2.42	0.84 ^a

^a Measured by Du Pont Polyester Technology.

^b Measured by Shell Chemical Company.

Dynamic mechanical thermal analysis

The dynamic mechanical measurements were conducted on a Polymer Laboratories Ltd DMTA. Rectangular samples 10 × 5 mm and of approximately 400 μm thickness were clamped using a single cantilever mode of action and knife-edge clamping arrangement. Clamping torque was 40 N. Temperature scans were performed from -120 to +150°C. The scanning frequencies were 0.3, 3, 10, 20, and 30 Hz. The samples were reclamped at low temperatures to minimize slippage.

RESULTS AND DISCUSSION

Following accepted convention,^{8,10,16} the transitions of PET are stated as α and β with decreasing temperature, and similarly, the transitions in PEN are stated as α, β*, and β. PTT, with two distinct transitions, has a greater similarity to the profile of PET; therefore, as in PET, the higher temperature transition will be termed α and the lower β.

α-Relaxation

The α-relaxation is associated with the onset of cooperative motion. Therefore, as can be seen in Figure 2, it is unsurprising that the α-relaxation temperature decreases with increasing chain flexibility (i.e., PEN > PET > PTT) with PEN being the most rigid of the homologs.

The activation energies of a relaxation process can normally be determined from plots of log frequency against reciprocal temperature using the Arrhenius equation:

$$\log f = A + \left(\frac{-E_a}{2.303RT} \right)$$

where f is the frequency used in the experiment, T is the temperature at which the $\tan \delta$ peak occurs, E_a is the activation energy, R is the gas constant, and A is a constant.

The problem with this approach with regard to the α-relaxation is that the Arrhenius approach by definition assumes that reciprocal temperature of the $\tan \delta$ peak will vary linearly with log frequency. For this to

be true, only one relaxation should occur during the transition. If more than one relaxation is present, the plot will be distinctly curved, consistent with a variation in the activation enthalpy as the glass transition is approached. To compensate for this effect various models have been developed such as that due to Williams, Landel, and Ferry (the WLF model), which predicts the variation of frequency with temperature.²¹ However, as can be seen in Figure 3, a simple Arrhenius plot shows a remarkable degree of linearity for the α-relaxations, sufficient enough for an accurate first estimation of the activation energy, data for which is given in Table II. Such linearity has been observed before.²²⁻²⁴ With regard to the activation

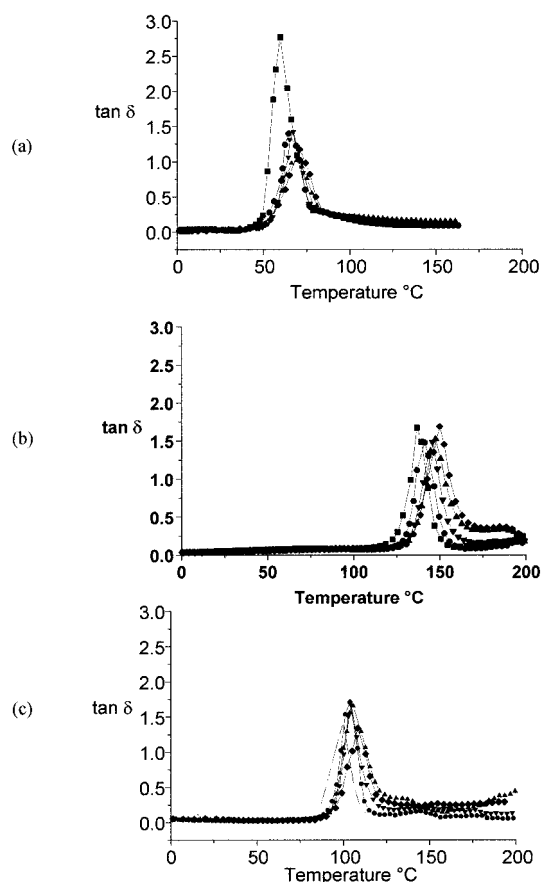


Figure 2 α Transition region of DMTA curves for (a) PTT, (b) PEN, (c) PET at 0.3 Hz (■), 3 Hz (●), 10 Hz (▼), 20 Hz (▲), and 30 Hz (◆).

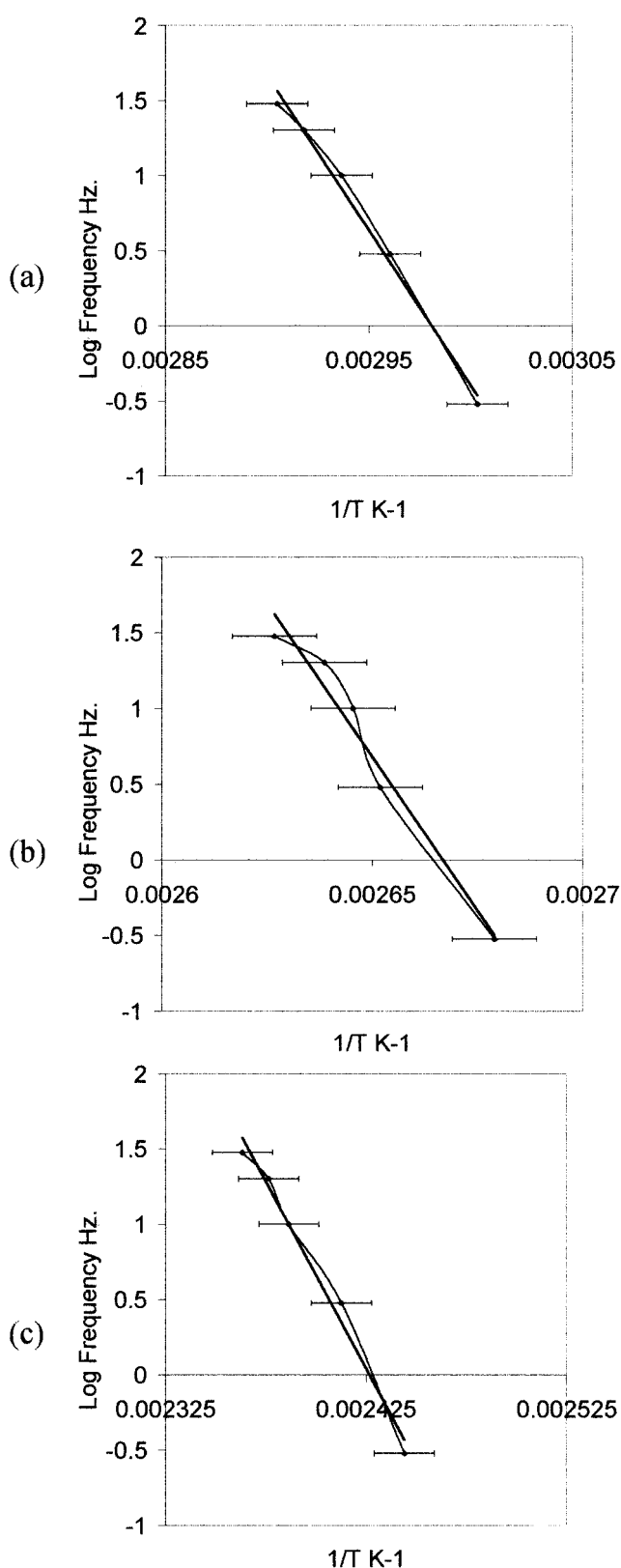


Figure 3 Arrhenius plots (α transition) for (a) PTT, (b) PEN, (c) PET.

energy, PET gives the highest activation energy of the three homologs at $775 \pm 77 \text{ kJ mol}^{-1}$, which is in good agreement with some literature values 753 kJ mol^{-1} ,²⁵

778 kJ mol^{-1} ,²³ but significantly higher than others, 273 kJ mol^{-1} ,²⁴ and 384 kJ mol^{-1} .²⁶ PEN gave the second highest activation energy at 475 kJ mol^{-1} , which is a little higher than the reported values 345 kJ mol^{-1} ,²⁴ and $350.4 \text{ kJ mol}^{-1}$,²⁶ and significantly higher than the $198.8 \text{ kJ mol}^{-1}$ reported by Canadas et al.²⁷ The activation energy of the PTT is lower than that of the PET or PEN at 393 kJ mol^{-1} , which is unsurprising considering the higher chain flexibility of PTT.

It has to be noted that the activation energy determined by the Arrhenius relationship varies with the frequency range over which it is measured, and could explain the discrepancies between the values determined in this study and some of those in the literature. However, because all activation energies in this study have been determined over the same frequency range, these values can be used in a comparable way as a function of composition. The low activation energy of PEN compared to the PET is opposite to what is expected due to the lower bulkiness of the terephthalate ring compared to the more bulky naphthalate group in PEN. It could be argued that this is due to the PET containing a higher level of residual crystallinity from the melt quench. However, density measurements show our quenching procedure gives a near amorphous film with a density of 1.3352 g cm^{-3} , exactly consistent with the literature value of amorphous density at 1.335 g cm^{-3} .²⁸ Although our results are in disagreement with Becker et al., who state that PEN has a higher activation energy than that of PET,²⁴ Bellomo and Lebey²⁶ state values that show that PEN has a lower value than PET—in agreement with our observations.

β^* -relaxation

The β^* -relaxation positioned at 110°C at 30 Hz is stated by others to be related to the out-of-plane motion of the naphthalate unit and the motion is stated to be cooperative to some extent.^{15,20} Therefore, on considering the results for the α -relaxation and the fact that the β^* is so closely related to the higher temperature transition (see Fig. 4), it could be possible that the α -transition is the final step in the onset of cooperative motion. Therefore, the rotational energy barrier of the α -transition reflects the completion of the

TABLE II
Summary of DMTA Data for All Three Polymers

	Tan δ max at 30 Hz (β)/ $^\circ\text{C}$	Activation energy/kJ mol^{-1}	Tan δ max at 30 Hz (α)/ $^\circ\text{C}$	Activation energy/kJ mol^{-1}
PTT	-51	70 ± 10	71	393 ± 40
PET	-17	79 ± 10	107	775 ± 77
PEN	-30	61 ± 10	150	475 ± 47

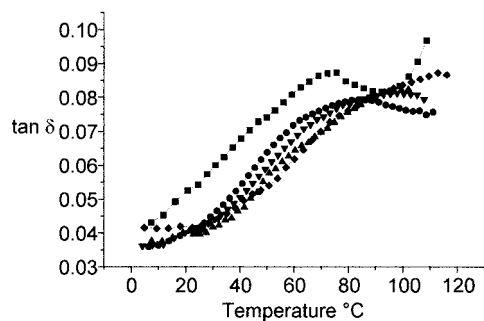


Figure 4 β^* transition region of DMTA curves for PEN, 0.3 Hz (■), 3 Hz (●), 10 Hz (▼), 20 Hz (▲), and 30 Hz (◆).

transition to full cooperative motion, rather than the overall transition between the glassy and liquid state. This explains to a certain degree the reason that we see a lower activation energy regardless of the bulkier naphthalene for the α -transition.

β -relaxation

Although the magnitude of the β -relaxation is very small, such that the PET and PEN peaks are similar, they can be differentiated at 30 Hz and the β -relaxation temperature decreases through the series PET > PEN > PTT, as shown in Figure 5; this is not the same order as that of the α -relaxation. This can be explained by following the hypothesized mechanism of the β -relaxation as stated by Maxwell and others.^{9,10,13,15} If the β -transition does indeed involve two relaxations—a lower temperature relaxation involving the carbonyl entities, and a higher temperature relaxation involving the C1–C4 phenyl ring flips—this then goes some way to explain the position of the PET and PEN β -relaxation in our study. As the PEN naphthalene relaxation occurs at a much higher temperature we can assume that the β -relaxation for PEN involves only the carbonyl moiety, this is consistent with that stated by Maxwell that the lower temperature side of the β -relaxation involves the carbonyl.^{9,10} In contrast to the positions of the PET and PEN relaxations, PTT has a much broader relaxation that occurs at a lower temperature. This is also consistent with the hypothesized mechanism stated by Maxwell and others,^{9,10,13,15} as the additional flexibility of the aliphatic segment would allow the carbonyl entities to relax at a lower temperature.

With regard to the activation energies, it is immediately obvious that there is a degree of nonlinearity in the Arrhenius plots (Fig. 6). This is not altogether unexpected for PET and PTT due to the breadth of the transition (consistent with two underlying processes), although undoubtedly there is also a contributing experimental uncertainty due to the small magnitude of the $\tan \delta$ peak; this uncertainty is quantified in Table

II. However, the activation energies for PET and PEN are consistent with those found in the literature; Ito states the lowest activation energy for PET at 56.9 kJ mol^{-1} with Maxwell et al.¹⁰ at 70 kJ mol^{-1} and Aref-Azar et al.²³ at 100 kJ mol^{-1} . The values stated for PEN by Hardy et al.¹⁶ are within the range of $45\text{--}49 \text{ kJ mol}^{-1}$ for dynamic mechanical and dielectric spectroscopy, respectively. These authors suggest that the higher activation energy for the PET vis-à-vis PEN is due to the aromatic and carbonyl both relaxing in the case of the PET and only the carbonyl relaxing for the PEN, as the bulky naphthalene group of the PEN is more associated with the β^* -relaxation. However, the activation energy for PTT lies between that of PET and

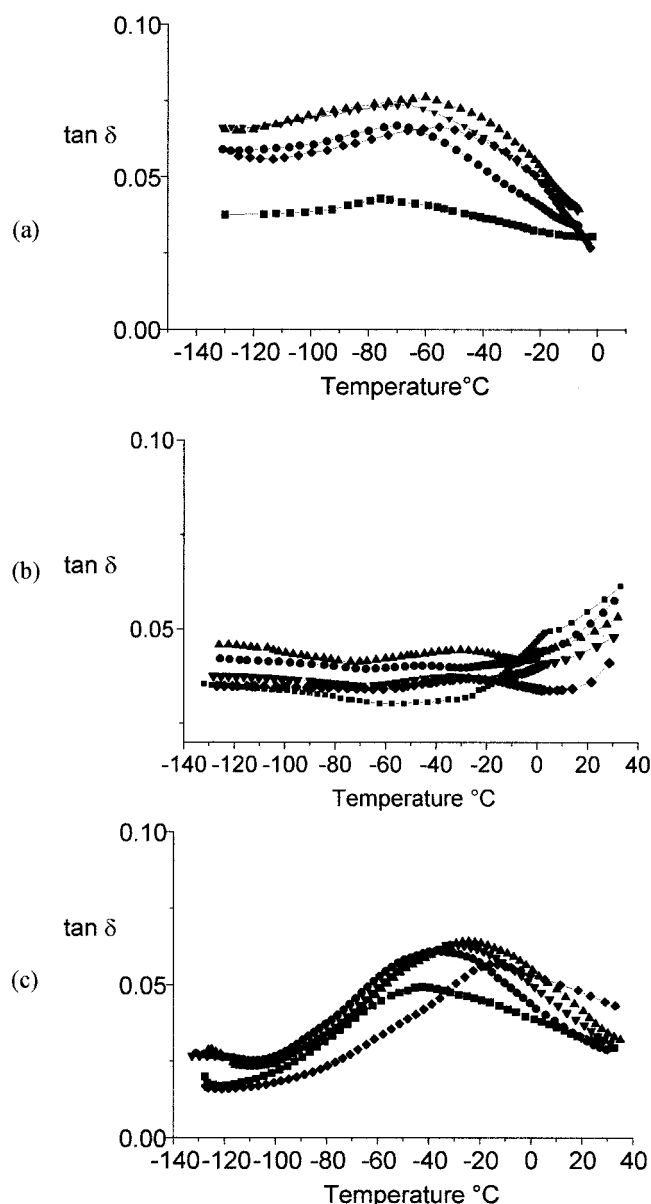


Figure 5 β Transition region of DMTA curves for (a) PTT, (b) PEN, (c) PET; 0.3 Hz (■), 3 Hz (●), 10 Hz (▼), 20 Hz (▲), and 30 Hz (◆).

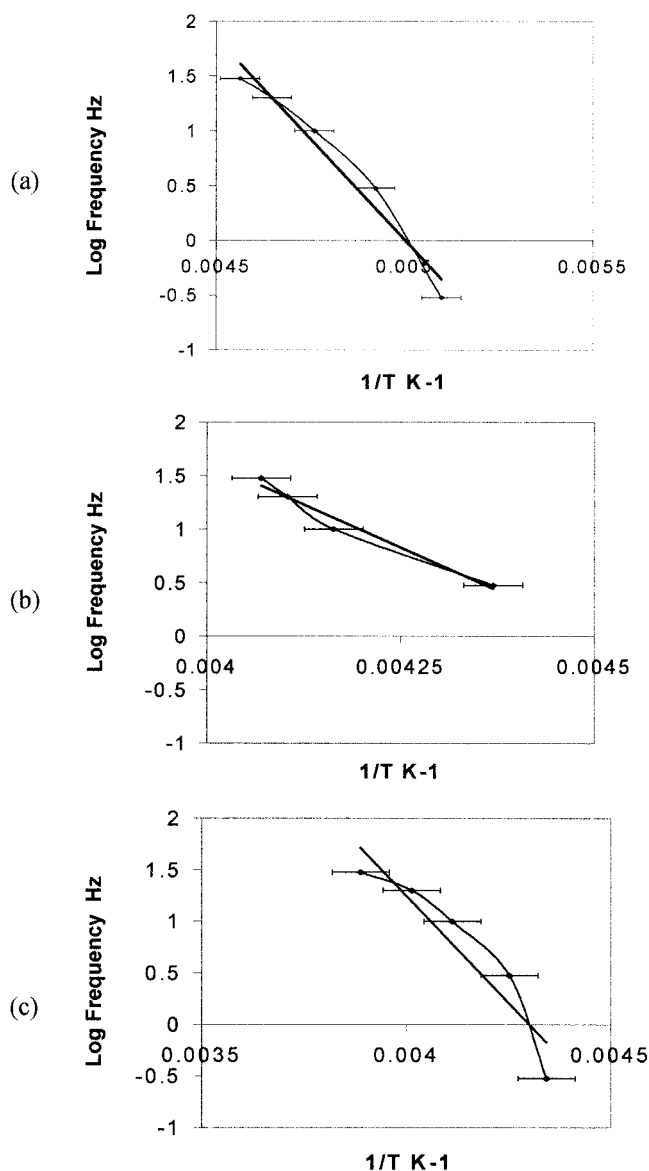


Figure 6 Arrhenius plots (β transition) for (a) PTT, (b) PEN, (c) PET.

PEN, but within the given error there is, in fact, very little difference between all three.

CONCLUSIONS

The added flexibility of the PTT backbone lowers the temperature of the β - and α -transitions relative to PET and PEN. The results suggest that the β -transition process consists of at least two relaxations for PET and PTT, as shown by the increase in the breadth of the relaxation. The β -relaxation for PEN occurs at a similar temperature to that of PET, although the relaxation occurs over a narrower temperature range. Furthermore, the Arrhenius plots for the β -relaxation for all three polymers do not

show the degree of linearity expected for a simple one-process transition. In contrast, Arrhenius plots for the α -relaxation show a remarkable degree of linearity; the activation energies for the transition are lowest for PTT and highest for PET. The results, therefore, appear to support the hypothesized mechanism of Maxwell et al. and others,^{9,10,13,15} in that the β -transition involves the relaxation of the carbonyl entity and the aromatic C1–C4 ring flips for both PTT and PET, and only the relaxation of the carbonyl for PEN. The β^* - and α -transitions for all three seem to be cooperative in nature, which is consistent with that stated by others.

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