Study of multiple relaxations in PEBAX, polyether block amide (PA12 2135 block PTMG 2032), copolymer using the thermally stimulated current method

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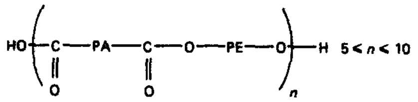
The relaxation behaviour of PEBAX (PA12 2135 block PTMG 2032) copolymer studied by the thermally stimulated current (t.s.c.) method is presented. The phases of PEBAX having soft segment, poly(tetramethylene glycol) (PTMG) ($\bar{M}_n = 2032$), and hard segment, polyamide (PA12) ($\bar{M}_n = 2135$), are separated at −65°C and 19°C for a raw sample, showing that a well defined phase separation occurs in this system. T.s.c. spectra of annealed samples indicate that domain morphology may be affected by thermal treatment. A comparison is made of rapid and slow cooling t.s.c. on hard-segment molecules. The modes β_{PTMG} and β_{PA} have been analysed by the fractional polarization method. Maximum energy observed for modes β_{PTMG} and β_{PA} is 1.27 eV at −61°C and 1.40 eV at −9°C. The elementary processes that constitute the modes β_{PTMG} and β_{PA} obey a compensation law with $T_C = 240$ K and $\tau_C = 4.1 \times 10^{-3}$ s for mode β_{PTMG}, and $T_C = 403$ K and $\tau_C = 2 \times 10^{-8}$ s for mode β_{PA}.

(Keywords: multiple relaxations; PEBAX; thermally stimulated current)

INTRODUCTION

The overall structure of PEBAX copolymer is



$$\mathrm{HO}\left(-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{PA}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{PE}-\mathrm{O}-\right)_n\mathrm{H} \quad 5<n<10$$

where PA and PE are the hard and soft segments respectively. On choosing conveniently the polyamide (PA6, PA66, PA11, PA12, etc.) and the polyether sequences (PEG, PPG, PTMG, etc.), the mechanical, chemical and thermal properties of the polyether block amide copolymer can be changed. The nature of the polyamide sequence has an influence on melting point, specific gravity and chemical resistance. The nature of the polyether sequence controls hydrophobicity and antistatic performance[1]. The present study deals with the molecular properties of PEBAX whose hard segment is PA12 ($\bar{M}_n = 2135$) and whose soft segment is poly(tetramethylene glycol) ($\bar{M}_n = 2032$). At service temperature, the soft segment PTMG is above its glass transition and is semicrystalline, and the hard segment PA12 is below its glass transition and is also semicrystalline. The unique properties of the copolymer are directly related to its two-phase microstructure, with the hard domain acting as a reinforcing filler and as a thermally reversible crosslink. The presence of three-dimensional hydrogen bonding within the hard domain leads to the usually strong hard-domain cohesion[2]. The primary force for domain formation is the strong intermolecular interaction between the amide units, which are capable of forming inter-amide hydrogen bonds. The soft segment is responsible for the rigidity of the copolymer. Factors that control the degree of microphase separation include copolymer composition, block length, crystallizability of either segment and the method of sample fabrication[3–5]. If the hard segment is amorphous, it will have a high glass transition, but if it is semicrystalline it will have a high fusion temperature[6]. Phase separation plays an important role in determining the dielectric and inelastic properties of the copolymer[7]. The thermally stimulated current (t.s.c.) method is well suited for the phase segregation followed by the observation of glass transitions.

THEORY

The t.s.c. technique is a method of studying the molecular interaction in a compact phase. This method was introduced by Bucci *et al.* in 1964[8]. Material under study is placed in an electrode system of a cryostat, which is kept under a vacuum of 10^{-6} mmHg. Dry helium is supplied to improve heat transfer and minimize the temperature gradient[9]. The sample is then polarized by an external d.c. field. This polarization gives rise to dipolar orientation as well as space-charge displacement, which can contribute to the development of an internal field[10]. The sample is cooled down to liquid-nitrogen temperature, at which point it is short-circuited through a sensitive electrometer. The specimen is then heated at a controlled linear rate. The reorientation of the dipoles to their random configuration during heating produces an electrical current peak recorded as a function of temperature given by

$$I(T) = \frac{N\mu^2\alpha E_{\mathrm{p}}}{kT_{\mathrm{p}}\tau_0}\exp\left[\frac{-\Delta H}{kT} - \frac{1}{b\tau_0}\int_{T_0}^{T}\exp\left(\frac{-\Delta H}{kT}\right)\mathrm{d}T\right] \quad (1)$$

where N is the dipole concentration, μ the dipole moment, α the factor for the freedom of dipole orientation, b the

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linear heating rate, E_p the polarization field, T_p the polarization temperature, ΔH the activation energy and k is Boltzmann's constant.

The global spectrum gives information about the number and amplitudes of the relaxations. To analyse the values of the activation energy and the relaxation time at different temperatures, a fractional polarization technique has been applied. The sample is polarized at temperature T_p during time t_p (2 min) to make the alignment of the dipoles perfect. The temperature of the sample under the field is lowered to $T_d = T_p - \Delta T$ (10 K). The sample is then short-circuited for 2 min to remove any stray surface charges. The temperature is again lowered to 80 K and the depolarization current is recorded. A series of spectra can thus be obtained[11-13]. The recorded $J(T)$ and $T(t)$ allow us to obtain $P(T)$, from which the relaxation $\tau(T)$ can be deduced by the relation

$$\tau(T) = P(T)/J(T) \tag{2}$$

The compensation phenomenon will take place if there is a linear relationship between $\ln \tau_0$ and ΔH (ref. 14). The Arrhenius equation

$$\tau = \tau_0 \exp(\Delta H/kT) \tag{3}$$

can be arranged as

$$\tau(T) = \tau_C \exp\left[\frac{\Delta H}{k}\left(\frac{1}{T} - \frac{1}{T_C}\right)\right] \tag{4}$$

The distribution of relaxation time will have only one τ_C at T_C. The value of T_C is calculated by the following expression:

$$\frac{1}{T_C} = \frac{\ln \tau_{01} - \ln \tau_{02}}{\Delta H_2 - \Delta H_1} \times 8.62 \times 10^{-5} \tag{5}$$

RESULTS AND DISCUSSION

Figures 1 and *2* show the glass transition of homopolymers PA12 ($\bar{M}_n = 2100$) and PTMG ($\bar{M}_n = 2000$) at 52°C and −74°C respectively. The t.s.c. spectrum of a raw sample (size 64×10^{-6} m^2, thickness 2.5 mm) of PEBAX (PA12 2135 block PTMG 2032) has been recorded in *Figure 3*, in which the respective phases of β_{PTMG} and β_{PA} are separated at −65°C and 19°C. At −29°C a new peak, in the form of shoulder, has appeared as a result of micro-Brownian motion. This type of shoulder is also visible in homopolymer PA when $\bar{M}_n > 2000$. The upper glass transition of PTMG (−12°C) may also be responsible for this shoulder in PEBAX. Heat treatment, such as heating the sample at 120°C for 1 h, annealing the sample (at 120°C for 24 h) or recrystallizing the sample after fusion, is done to obtain a better

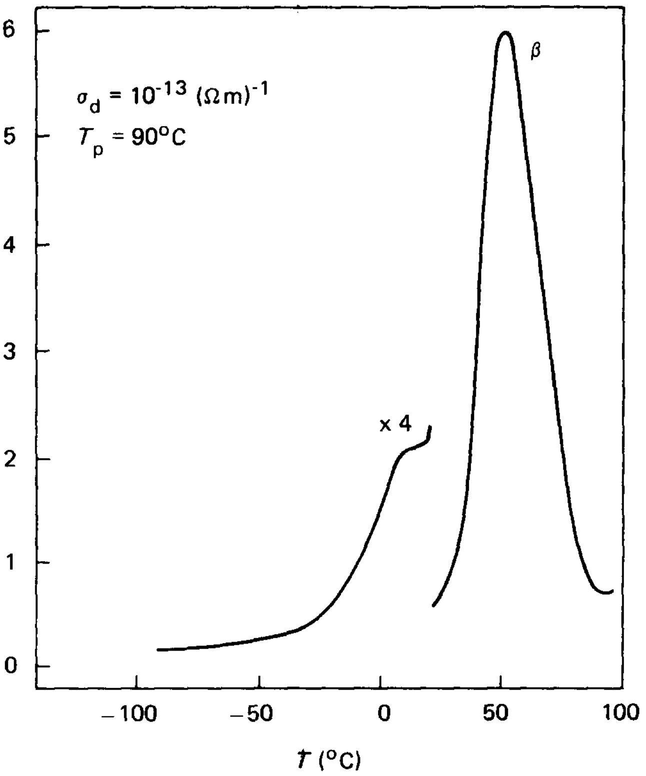

Figure 1 T.s.c. spectrum of polyamide, PA12 ($\bar{M}_n = 2100$)

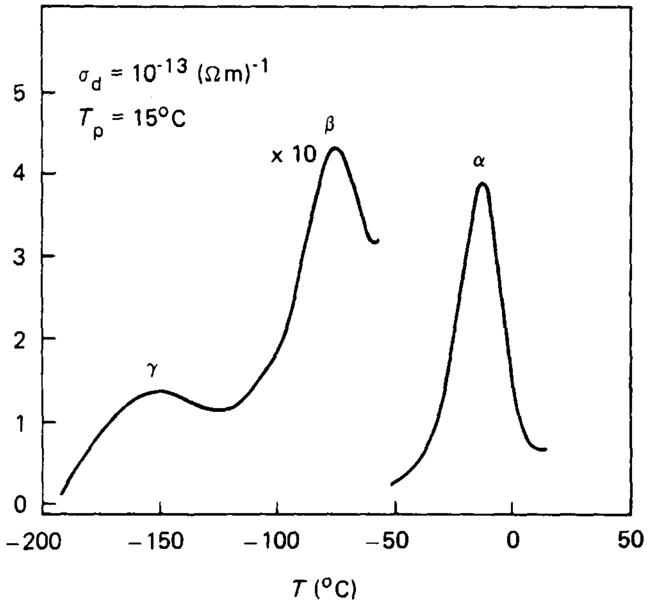

Figure 2 T.s.c. spectrum of poly(tetramethylene glycol), PTMG ($\bar{M}_n = 2000$)

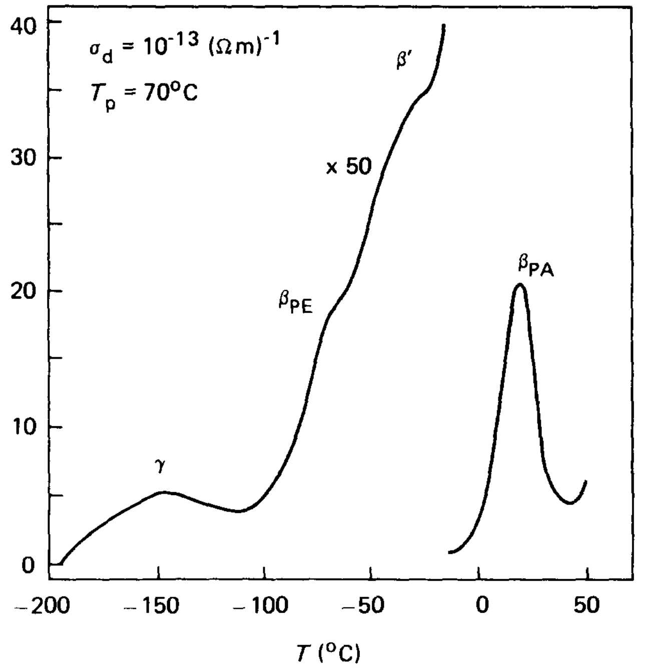

Figure 3 T.s.c. spectrum of PEBAX (PA12 2135 block PTMG 2032) copolymer

understanding of the phases of PEBAX. *Figures 4*, *5* and *6* indicate the spectra obtained under different conditions of heat treatment. The t.s.c. results are listed in *Table 1*. *Figure 7* represents t.s.c. spectra showing the effect of slow cooling after polarization for an annealed sample (at 120°C for 16 h) and a sample recrystallized after fusion.

Table 1 Phase separation of PEBAX (PA12 2135 block PTMG 2032) copolymer under different conditions

Condition	$T(\beta_{PE})$ (°C)	$T(\beta')$ (°C)	$T(\beta_{PA})$ (°C)
Raw	−65	−29	19
Heated at 120°C for 1 h	−62	−30	11
Annealed (at 120°C for 24 h)	−62	−30	11
Recrystallized after fusion	−62	−40	13

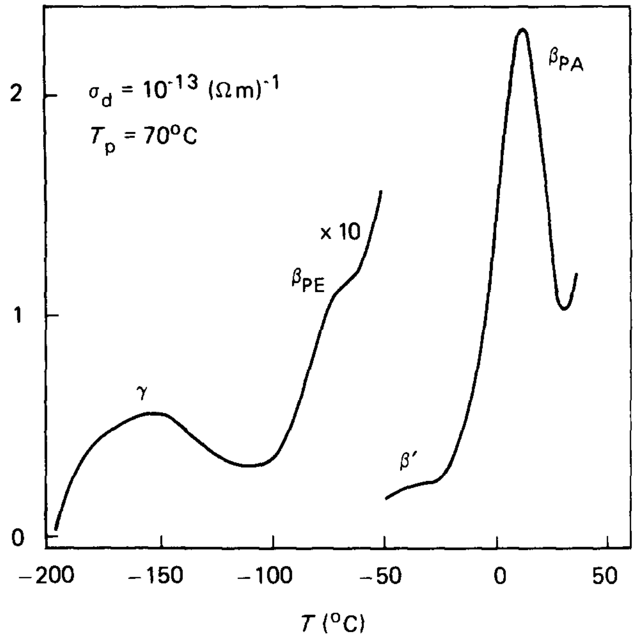

Figure 4 T.s.c. spectrum of PEBAX heated at 120°C for 1 h

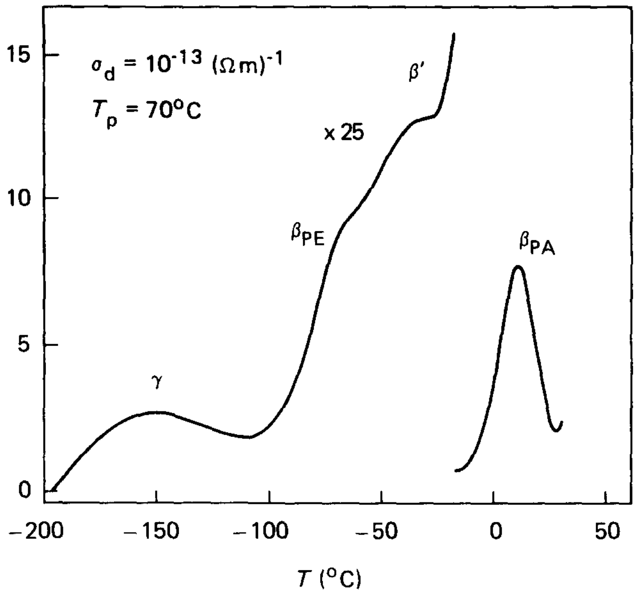

Figure 5 T.s.c. spectrum of PEBAX annealed at 120°C for 24 h

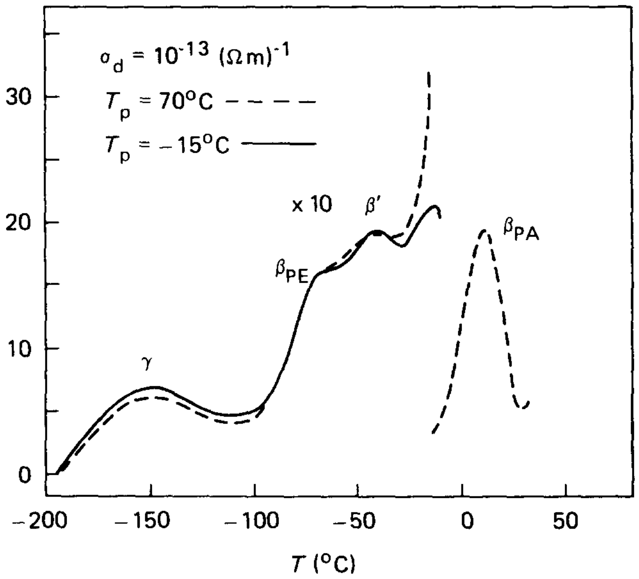

Figure 6 T.s.c. spectrum of PEBAX recrystallized after fusion

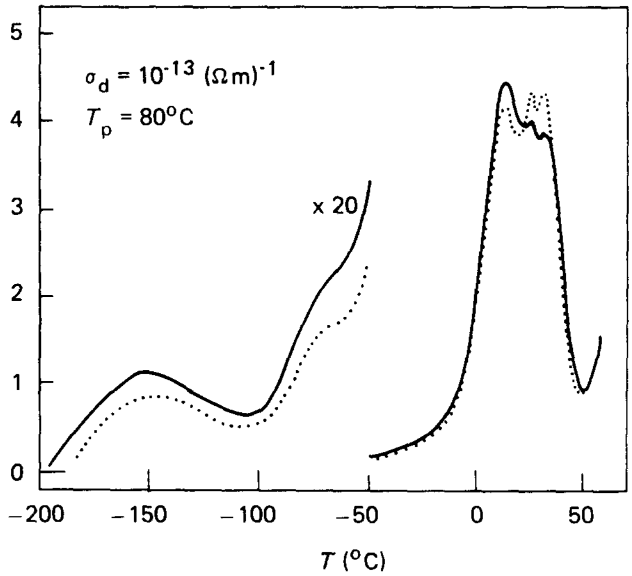

Figure 7 T.s.c. indicating the effect of slow cooling: ——, sample annealed at 120°C for 16 h; ·····, recrystallized sample

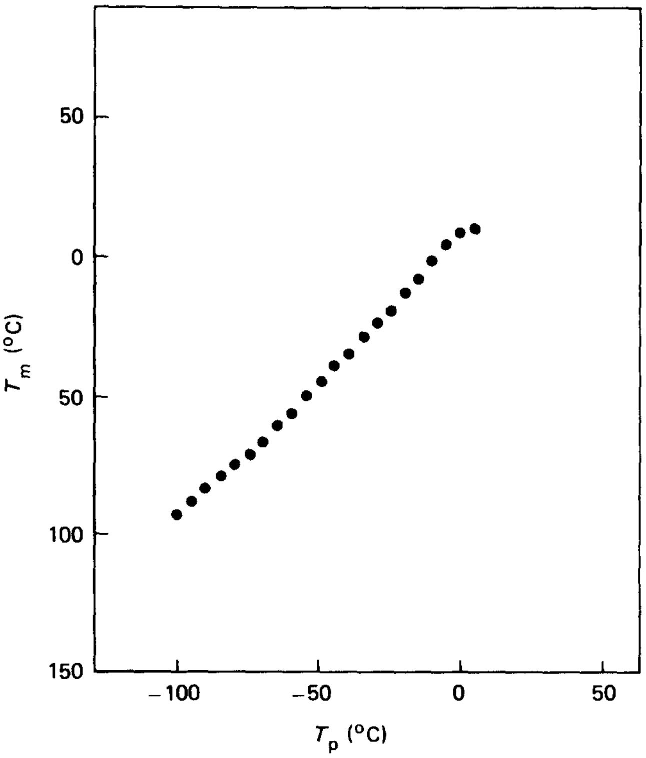

Figure 8 The variation of T_m as a function of T_p for PEBAX

The glass transition of the hard segment has been split into three parts when the temperature is lowered at a speed of 2°C min^{-1} after polarization. The variation of T_m as a function of T_p in *Figure 8* obtained by the fractional polarization method for the raw sample represents the existence of two modes of relaxation in PEBAX. The Arrhenius diagram (*Figure 9*) shows the presence of two modes β_{PTMG} and β_{PA} characterized by two compensation laws. All the parameters have been reported in *Table 2* and the results have been verified by plotting a diagram of $\ln \tau_0$ against ΔH (*Figure 10*).

CONCLUSION

The β_{PE} phase has practically the same characteristics as that of PTMG homopolymer. The larger distribution of activation energy in PA homopolymer has been diminished in the β_{PA} phase of PEBAX. The PEBAX with a long sequence of PA ($\bar{M}_n > 2000$) has a more disordered amorphous PA phase than that of PEBAX with a short sequence of PA ($\bar{M}_n < 2000$). The increase in length and content of hard segment in a given chemical structure causes increasing deviation of the thermoelastic

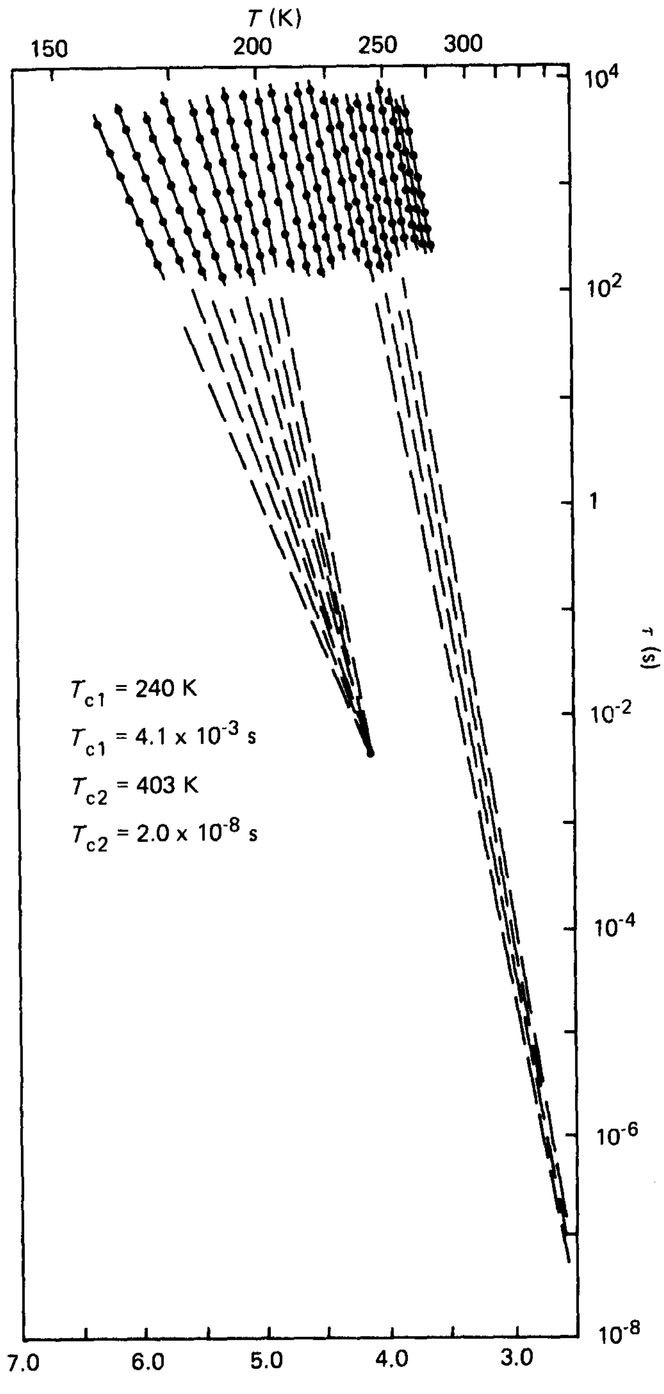

Figure 9 Arrhenius diagram of relaxation time isolated in PEBAX

Table 2 The parameters ΔH and τ_0 of Arrhenius peaks isolated at T_m in PEBAX (PA12 2135 block PTMG 2032) copolymer

Peak	T_p (°C)	T_m (°C)	ΔH (eV)	τ_0 (s)	Remarks
1	−100	−93	0.58	1.7×10^{-15}	C β_{PTMG}
2	−95	−89	0.62	4.2×10^{-16}	C β_{PTMG}
3	−90	−84	0.70	7.0×10^{-18}	C β_{PTMG}
4	−85	−79	0.74	1.3×10^{-18}	C β_{PTMG}
5	−80	−74	0.85	8.6×10^{-21}	C β_{PTMG}
6	−75	−70	0.95	8.7×10^{-23}	C β_{PTMG}
7	−70	−66	1.03	8.7×10^{-25}	C β_{PTMG}
8	−65	−61	1.27	1.1×10^{-29}	C β_{PTMG}
9	−60	−55	1.35	1.2×10^{-30}	
10	−55	−50	1.34	1.1×10^{-29}	
11	−50	−45	1.28	1.4×10^{-27}	
12	−45	−40	1.36	7.2×10^{-29}	
13	−40	−35	1.30	1.2×10^{-26}	
14	−35	−28	1.34	8.7×10^{-27}	
15	−30	−24	1.20	1.9×10^{-23}	C β_{PA}
16	−25	−20	1.32	3.9×10^{-25}	C β_{PA}
17	−20	−14	1.37	1.2×10^{-25}	C β_{PA}
18	−15	−9	1.40	6.5×10^{-26}	C β_{PA}
19	−10	−1	1.42	1.3×10^{-25}	
20	−5	4	1.38	4.3×10^{-24}	
21	0	9	1.24	3.2×10^{-21}	
22	5	10	1.32	2.3×10^{-22}	

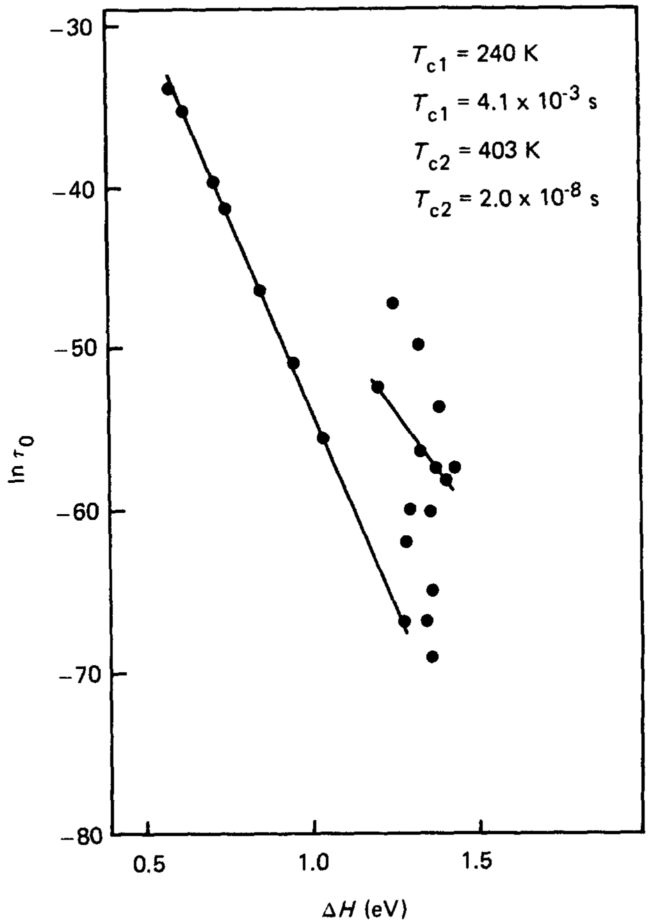

Figure 10 The variation of $\ln \tau_0$ as a function of ΔH for the relaxation times isolated in PEBAX

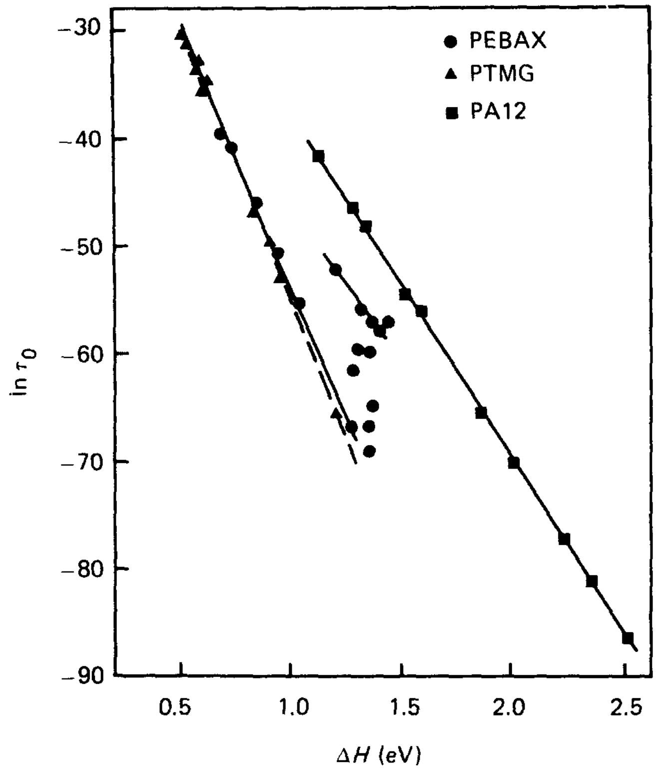

Figure 11 Comparison between homopolymers (PA12 12 000, PTMG 2000) and copolymer (PEBAX) representing the variation of $\ln \tau_0$ as a function of ΔH

properties of PEBAX. Micro-Brownian motion is only occurring in the elastomeric phase. The characteristics do not shift significantly when the copolymer composition varies, which is obviously a good indication of the existence of a well defined two-phase structure.

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