Journal of Thermal Analysis Vol. 46 (1996) 773-783

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

STUDY OF TEMPERATURE TRANSITIONS IN SOLID POLY(OXYMETHYLENE) BY THERMAL ANALYSIS METHODS

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Abstract

Poly(oxymethylene)s with different molecular mass and chemical structure were studied using DSC, dynamic mechanical relaxation, thermomechanical analysis, and thermogravimetry.

Molecular mobilities of two types were found in the amorphous phase of poly(oxymethylene). Unconstrained chains of poly(oxymethylene) soften at –70°C and then amorphous chains with different restraints from the crystalline phase are successively activated in a wide temperature interval.

Keywords: dynamic mechanical properties, glass transition, polyoxymethylene, rigid amorphous phase

Introduction

Highly crystalline flexible chain polymers are complex heterogeneous systems composed of amorphous and crystalline phases of different order. Despite simple chemical structures most of these polymers are characterized by multiple thermal transitions having positions and intensities which depend on the thermal prehistory, regularity, and molecular mass of the polymer. In most cases, assignment of a transition to a definite type of intra- and intermolecular motion remains controversial. Even the glass transition temperature remains uncertain in these systems. This is also true of poly(oxymethylene) (POM).

Boyer [1] systematized the data of various authors and suggested the following classification of temperature transitions in crystalline polymers:

1) transition at $T < T_g(L)$, which is low-sensitive to crystallinity, is associated with local motion of several carbon atoms (for POM $T < -70$°C);

2) transition at $T_g(L)$, which is glass transition of unconstrained amorphous regions, slightly depends on crystallinity (for POM –70 – –20°C);

0368–4466/96/ $ 5.00

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3) transition at $T_g(U)$, which is associated with glass transition in amorphous regions constrained by crystallites, is sensitive to crystallinity (for POM –10 – –50°C);

4) transition at $T_{\alpha c}$, motion in crystalline regions, which is associated with premelting (for POM 100–135°C).

Wunderlich *et al.* [2] believe that for POM T_g = –83 °C, whereas, according to Bohn [3], T_g of this polymer is –30°C. Stehling and Mandelkern [4] attributed an anomaly of the coefficient of linear expansion at –85°C to glass transition.

The authors of [5] observed four anomalies on the mechanical relaxation spectrum of the homopolymer of oxymethylene and its copolymers and made the following assignment: the peaks at –220 and –98°C were assigned to the motions in imperfect crystalline regions, the peak at –68°C was assigned to the motion of short segments in disordered regions, whereas the peak at –3°C was attributed to the motion of long segments, glass transition. Note that the data on the use of DSC for determining T_g are rather limited.

Thus, in earlier works two regions: –85±10°C and –15±10°C are reported as temperature regions of glass transition of POM.

The data show that the difficulty of interpreting the thermal transitions in highly crystalline polymers is associated with the complexity of their structure arising due to different disturbances of the crystalline order.

Presently, it is recognized that the two-phase structure model, which was widely used previously, does not provide a sufficient explanation of the observed multiplicity of anomalies. The three-phase structural model suggested by Wunderlich *et al.* [2] on the basis of calorimetric measurements turned out to be more fruitful.

For a series of crystalline polymers, these authors found that the dependence of specific heat on the degree of crystallinity deviates from additivity. For most polymers, they observed positive deviations of the heat capacity from additivity associated with premelting or defect formation. In contrast, POM is characterized by negative deviations. According to Wunderlich *et al.* [2], this implies that a fraction of the polymer does not manifest itself in either in the glass transition or melting. This fraction was called "rigid-amorphous phase", and it was shown that its content remains constant up to the melting point. This approach makes it possible to establish the quantitative relationship between the parameters of crystalline and amorphous phases.

The idea about the occurrence of a rigid-amorphous phase is unquestionable associated with the concept of an amorphous phase with restraints in mobility in terms of the Boyer classification [1]. However, according to Boyer, these phases are characterized by higher T_g, whereas Wunderlich believes that they soften only in the region of melting.

The objective of this work was to find and identify thermal transitions in POM using various methods of thermal analysis and to interpret them in terms of the three-phase model suggested for crystalline polymers.

Experimental

As subjects of investigation we used samples of Delrin® (POM) of three different molecular masses: 30×10^3– (D-1), 41×10^3 – (D-2), and 66×10^3 – (D-3) and Celcon®, a random copolymer of oxymethylene containing 2.5% ethylene-oxide units with MM $=41\times10^3$ (C-I) as granules, fibers, and bars.

The dynamic mechanical properties of the samples were studied using a version of the resonance method related to transverse oscillations of a vertically positioned fiber 0.2 mm in diameter and 30 mm in length in the temperature range from –160 to 200°C. The resonance oscillation frequency (f_r) was varied from 400 to 40 Hz. Young's modulus was calculated according to the formula

$$E' = 4\pi^2 lmf_r/S$$

where l and S are the length and cross-sectional area of the fiber, and m is the weight of the load.

The error of the values of E' is determined by the error in the measurements of geometric dimensions of the fiber and is equal to ±10%. We assumed that the dimensions of the fiber did not change through the whole temperature range examined. The error was primarily due to the error in measuring f_r, which was rather small (±0.1 Hz). Hence, the transitions in temperature dependences of E' were identified with high accuracy. The mechanical loss tangent ($\tan\delta$), was calculated from the width of the resonance curve Δf at the $1/\sqrt{2}$ of the maximum

$$\tan\delta = \Delta f/f_r$$

The error in the determination of $\tan\delta$ does not exceed 2%. Calorimetric studies were carried out using a Perkin-Elmer DSC-7 thermal analyzer in an atmosphere of helium at the temperature range –150 – +220°C at scanning rates of 20 and 40 K min^{-1}. The sample weights were 10–15 mg.

Thermomechanical and thermogravimetrical curves were obtained using a Mettler TA 3000 thermoanalytical complex under the following conditions:

1) TMA-40 measuring cell; Range: –100 – +160°C; Heating rate: 20 K min^{-1}; Purge gas: helium (100 $\text{cm}^3\ \text{min}^{-1}$); Load: 0.5 N (penetration)

2) TG–50 Thermobalance; Range: 30–280°C; Heating rate: 20 K min^{-1}; Purge gas: air (150 $\text{cm}^3\ \text{min}^{-1}$)

Results and discussion

Figure 1 shows typical DSC heating (1) and cooling (2) traces and a thermogravimetric curve (3) for the studied samples. The latter curve points out that no degradation of the polymers occurs during DSC studies.

Calorimetric study of all the samples indicates the following transitions: glass transition in the region of –70°C and melting, which appears at 80°C as a broad forearm with the melting point in the vicinity of 180°C. The characteristics of these transitions for different samples are listed in Table 1. In the case of POM, T_m and the degree of crystallinity (α) are strongly dependent on thermal prehistory of a polymer [4, 5]; therefore, Table 1 presents data obtained for the samples, which had been cooled from melt at a rate of 200 K min^{-1}.

Table 1 shows that the values of T_g and T_m of Delrins with different molecular mass differ insignificantly. Celcon has the same T_g as Delrins, whereas its T_m is markedly lower. The degree of crystallinity (α) appreciably decreases with an increase in MM of Delrin and on going to Celcon.

Let consider the dynamic mechanical properties of the polymers. Figure 2 (a–d) shows E' and tan δ temperature dependences for the D-1, D-2, D-3, and C-1 samples. As can be seen, all the polymers in the solid state are characterized by existence of four transitions designated by I, II, III, and IV.

Transition I at –120°C has a small intensity. For POM, this transition was also reported in [5]. The hypothesis concerning its nature will be given below.

The most intense transition II we observed at a higher temperature where the DSC heating traces of the studied samples show a jump in heat capacity associated with the glass transition. This allows us to assign transition II to POM glass

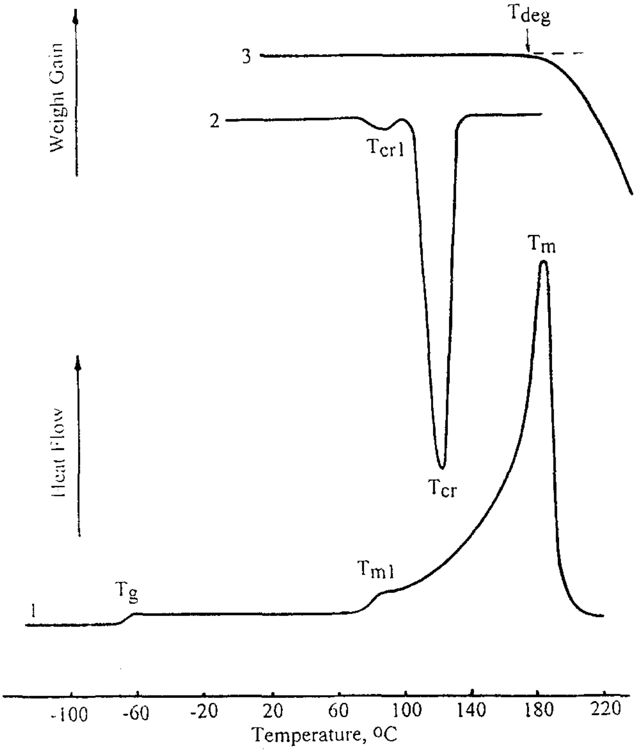

Fig. 1 Typical DSC (1) heating and (2) cooling curves and (3) TGA curve of POM

Table 1 DSC characteristics of quenched POM samples (heating rate 40, cooling rate 20°C min^{-1})

Sample	T_g/°C	T_m/°C	Q_m/J g^{-1}	α^*/%	T_{cr1}/°C	T_{cr2}/°C	Q_{cr1}/J g^{-1}
D–1	–68	185	192	59	147	93	184
D–2	–67	181	185	57	148	92	183
D–3	–69	184	179	55	144	94	160
C–1	–69	170	168	52	145	85	153

*Q_m^o = 326 J g^{-1} [6]

transition. It should be noted that as the molecular mass is increased in a series of Delrins, the intensity of transition II grows.

Transition III, which is characterized by small intensity, is observed in a wide temperature interval from –30 to 70°C. Unfortunately, DSC is insensitive to this transition. An increase in MM of a series of Delrins and, especially on going to Celcon, leads to an increase in the intensity of transition III. The DSC data show that α decreases in this series (Table 1); therefore, as similar to transition II, transition III is associated probably with the mobility in the amorphous phase of POM.

According to the three-phase model for crystalline polymers containing amorphous regions of two types, transition II at –70°C may be related to softening of POM chains unrestrained by the crystalline phase and transition III, which occurs within a wide temperature interval, to successive activation of amorphous chains with different restraint from the crystalline phase. Thus, conclusion about softening of the rigid-amorphous phase in POM is more likely corresponds to the Boyer classification. According to Boyer, these regions are characterized by higher T_g in comparison with glass transition of normal amorphous regions. Hence, above 70°C, both amorphous phases are softened.

As shown by the DSC and DMA data, melting of quenched POM starts above 80°C as melting of the most small and imperfect crystals. However, there is also a transition IV in the temperature range 100–150°C (i.e. some 30°C below the melting point) which is normally related to the α-relaxation transition in crystalline phase of POM [7–9].

Annealing in the region of 80–100°C allows us not only to shift the onset of POM melting toward higher temperatures (according to DSC data) but also to change the ratio between the soft and rigid fractions of the amorphous phase due to melting and recrystallization of these crystallites. Comparison between the first and second heating of D-3 shows (Fig. 2c) that annealing of the initial fibers causes a decrease in the share of the constrained portions in favor of unconstrained amorphous chains. This is evidenced by a decrease in the intensity of transition III and by an increase in the intensity of transition II. Thus, comparison of the peak intensities on the tan δ–T curves before and after annealing

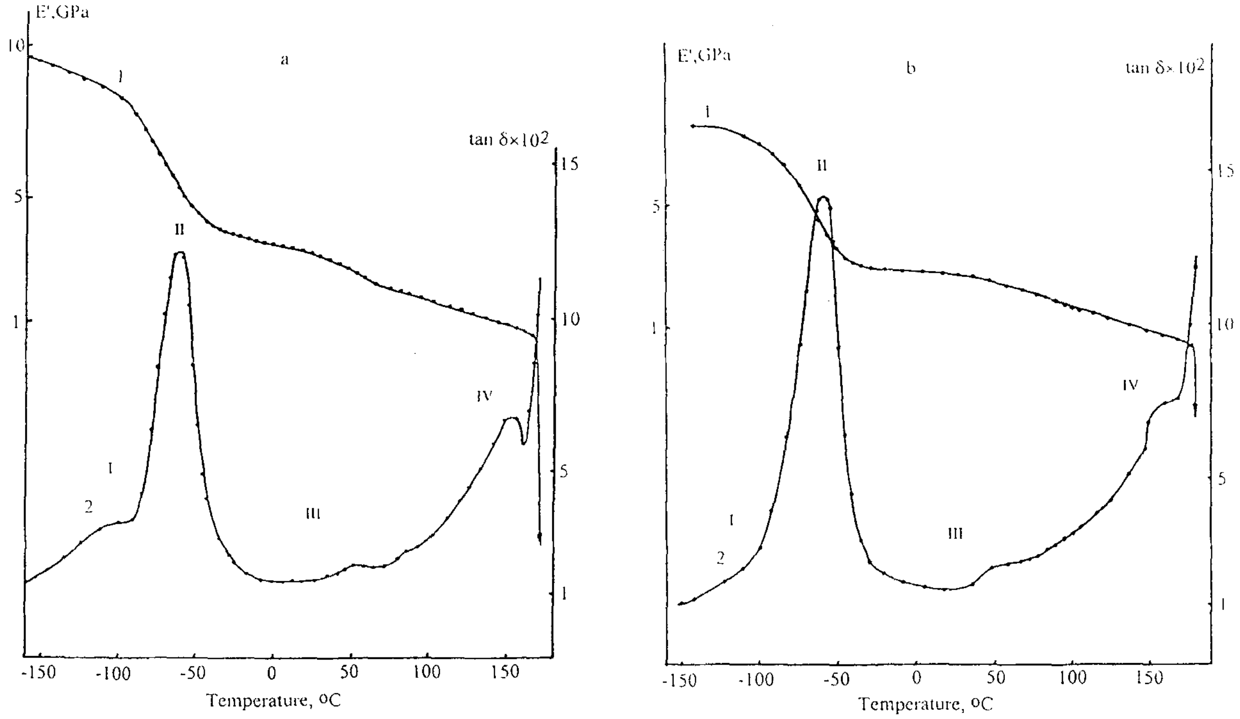

Fig. 2a,b Temperature dependences of (1, 3) Young's modulus *E'* and (2, 4) mechanical loss tangent (tan δ) for (a) D-1 and (b) D-2 fibers. 1 and 2, the initial fibers; 3 and 4, the annealed fibers

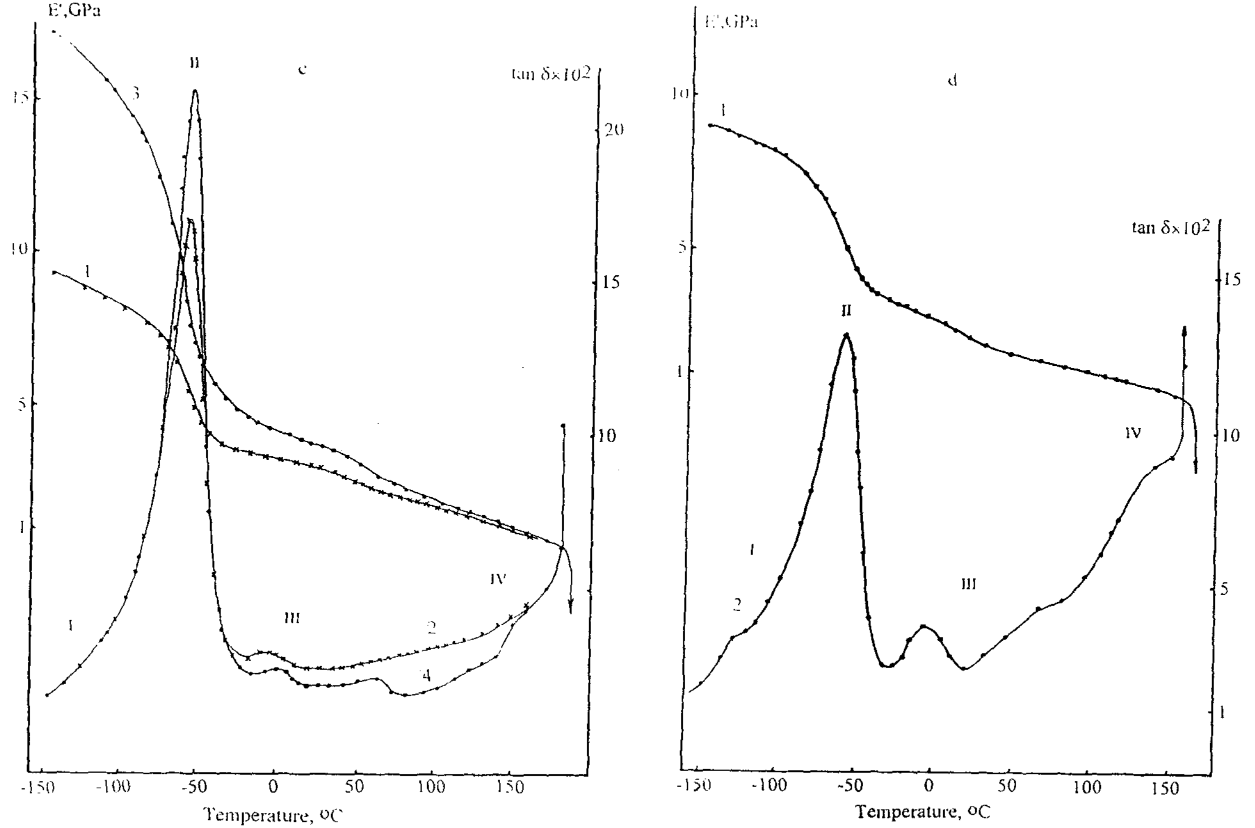

Fig. 2c,d Temperature dependences of (1, 3) Young's modulus E' and (2, 4) mechanical loss tangent (tan δ) for (c) D-3, and (d) C-1 fibers. 1 and 2, the initial fibers; 3 and 4, the annealed fibers indicates that the share of unconstrained amorphous chains increases by 25% on annealing.

The suggested interpretation of the transitions identified by the DSC and DMA methods agrees well with the results of thermomechanical measurements. The heating traces of the initial samples are almost similar (Fig. 3): after steady expansion a plateau is observed in the temperature range 20–90°C followed by a sharp rise. The coefficient of thermal linear expansion (β) virtually does not change up to the temperatures of the onset of the plateau, its minimum is observed in the region of the plateau, then β starts to sharply increase. On repeated heating, no plateau is observed, β remains constant up to 100°C and then grows sharply.

Figure 3 shows that for POM the change in β in the region of transition II is insignificant. In addition, the TMA curve in the region of transition II displays a plateau and abnormal deviation of β from the linear dependence on first heating, which were absent on repeated heating or after long annealing of the initial samples at 70°C (temperature at the middle of plateau). This shape of TMA curves of first heating is apparently associated with relaxation of strains, which appear during sample molding. Such relaxation becomes possible because of softening of the rigid amorphous phase of POM.

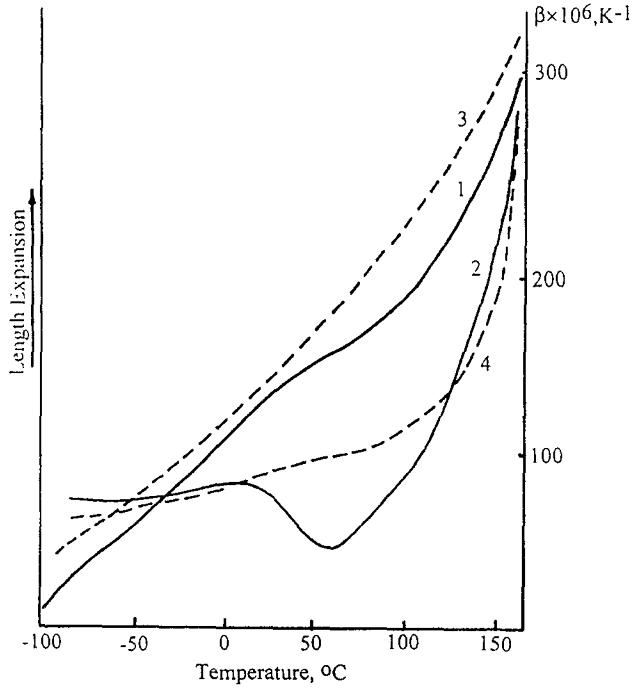

Fig. 3 Typical TMA curves (1, 3) and temperature dependences of β (2, 4) for POM. 1 and 2, initial samples; 3 and 4, annealed samples

The sharp rise on the TMA curve of the first and repeated heating in the region of 100°C corresponds to transition IV on the dynamic mechanical curves and to the onset of melting of the DCS traces.

Thus, from these experimental data we may conclude that two types of molecular mobility exist in amorphous phase of POM. Unconstrained chains of POM soften at –70°C and then successive activation of portions of amorphous chains with different restraints takes place.

In summary, it seems appropriate to compare the behavior of POM with that of the polymers with similar chemical structures and to make an effort to determine the generality of these conclusions. The characteristics of the polymers chosen for comparison are summarized in Table 2 and the generalized dependences of dynamic mechanical characteristics are shown in Fig. 4.

The temperature dependences of *E*′ and tan δ for all these polymers (Fig. 4) display transition I at –120°C. For the first five polymers, which monomer unit contains ether bonds –(O)– along with –CH$_2$– groups, one more transition II is observed at –70°C. An increase in the number of –CH$_2$– groups in the monomer

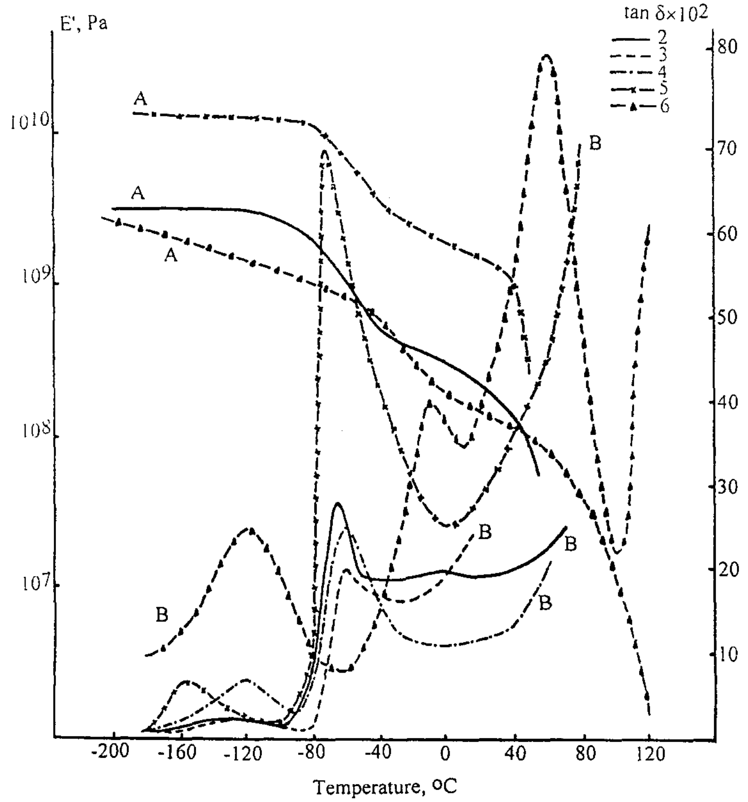

Fig. 4 Temperature dependences of (A) shear modulus and (B) tan δ for a series of flexible chain crystalline polymers. Designations of polymers and references are given in Table 2

Table 2 Melting temperature and degree of crystallinity for series of flexible chain crystalline polymers

	Polymer	Chemical structure	T_m/°C	α/%	References
1	poly(oxymethylene) (POM)	$-[CH_2O]_n-$	180	~60	[7–9]
2	poly(oxyethylene) (POE)	$-[(CH_2)_2O]_n-$	70	~90	[10]
3	poly(trimethyleneoxide) (PThMO)	$-[(CH_2)_3O]_n-$	30	~50	[11]
4	poly((tetramethyleneoxide) (PTMO)	$-[(CH_2)_4O]_n-$	35	~50	[11, 12]
5	poly(oxypropylene) (PPO)	$-[\underset{CH_3}{CH}-CH_2O]_n-$	50	~60	[13]
6	linear polyethylene (PE)	$-[CH_2]_n-$	130	~70	[14]

unit of the polymer causes an increase in the intensity of transition I. In the case of PE, the intensity of transition I is greatest, but, transition II is not observed.

Frequency-temperature relationships for transitions I and II of the five first polymers studied by the methods of dynamic mechanical and dielectric relaxation are shown in Fig. 5. The linear dependence of transition I in "log*f* – 1/*T*" coordinates makes it possible to assign transition I in these polymers to the

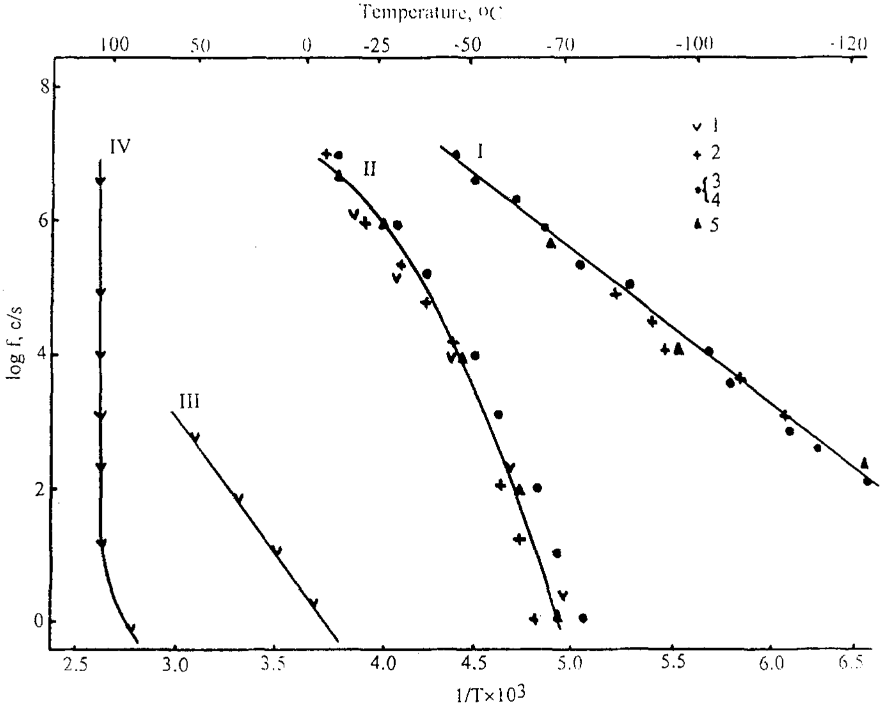

Fig. 5 Plots of log*f* *vs*.1/*T* for the dielectric and mechanical loss maxima of a series of flexible chain crystalline polymers. Designations of polymers and references are given in Table 2

process of local mobility, apparently, of $-CH_2-$ groups. Deviation of the "log$f$ – $1/T$" plot from linear dependence for transition II suggests that it is the glass transition. Moreover, it may be suggested that in the polymers with ether links, including POM, the glass transition is associated with its activation.

Conclusion

Thus, the study of the molecular mobility of POMs with different molecular mass and chemical structure showed that in the solid state POM is characterized by the following transitions:

1) at –120°C activation of local mobility of $-CH_2-$ groups occurs (transition I);

2) at –70°C an ether bond activates; therefore, cooperative motion of amorphous chains of POM with no restraints imposed by crystallites (transition II) becomes possible;

3) in the range –30 – +70°C softening of amorphous chains with different restraints from the crystallites (transition III) takes place;

4) There is the relaxation transition in crystalline phase of POM in the temperature range 100–150°C (some 30°C below the melting point), at 80°C melting of POM is beginning.

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This work has been supported by DuPont Company.

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