work. P.S. thanks the Swedish Institute, Stockholm, Sweden, for a travel grant making possible the combined measurement series in Prague and Uppsala. We are also grateful to the Swedish Natural Science Research Council for financial support of this program.

Registry No. Polystyrene, 9003-53-6.

References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: London, 1979.
(2) Ewen, B.; Richter, D.; Hayter, J. B.; Lehnen, B. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 233.
(3) Ewen, B.; Stuhn, B.; Binder, K.; Richter, D.; Hayter, J. B. *Polym. Commun.* **1984**, *25*, 133.
(4) Léger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(5) Marmonier, M. F.; Léger, L. *Phys. Rev. Lett.* **1985**, *55*, 1078.
(6) Deschamps, H.; Léger, L. *Macromolecules* **1986**, *19*, 2760.
(7) The overlap concentration, C^*, is defined here as $C^* = 3M/(4\pi R_g^3 N_A)$, where M is the molecular weight and N_A Avogadro's number.
(8) Amis, E.; Han, C. C. *Polymer* **1982**, *23*, 1042.
(9) Hwang, D. H.; Cohen, C. *Macromolecules* **1984**, *17*, 1679, 2890.
(10) Brown, W. *Macromolecules* **1985**, *18*, 1713.
(11) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379. *Ibid.* **1986**, *19*, 2002.
(12) Brown, W. *Macromolecules*, **1986**, *19*, 1083.
(13) Štěpánek, P.; Koňák, C.; Jakeš, J. *Polym. Bull. (Berlin)* **1986**, *16*, 67.
(14) Štěpánek, P.; Jakeš, J.; Koňák, C.; Johnsen, R. M.; Brown, W. *Polym. Bull. (Berlin)* **1987**, *18*, 175.
(15) Štěpánek, P.; Jakeš, J.; Brown, W. *J. Colloid Polym. Sci.*, in press.
(16) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(17) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428.
(18) Dautzenberg, H. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 61*, 83.
(19) Saeki, S.; Konno, S.; Kawahara, N.; Nakata, M.; Kaneko, M. *Macromolecules* **1974**, *7*, 521.
(20) Koňák, C.; Štěpânek, P.; Sedláček, B. *Czech. J. Phys.* **1984**, *A34*, 497.
(21) Brown, W. *Macromolecules* **1984**, *17*, 66.
(22) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(23) Stock, R. S.; Ray, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1393.
(24) Jakeš, J. *Czech. J. Phys.*, in press.
(25) Jakeš, J., submitted for publication.
(26) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(27) Cotton, J. P.; Nierlich, N.; Boué, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(28) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(29) Munch, J. P.; Candau, S. J.; Herz, J. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 971.
(30) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(31) Schaefer, D. W.; Lin, J. S. *Macromolecules* **1983**, *16*, 1015.
(32) *Beilstein* **1972**, 2, system no. 159.
(33) Munch, J. P.; Hild, G.; Candau, S. J. *Macromolecules* **1983**, *16*, 71.
(34) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.
(35) Takahashi, M.; Nose, T. *Polymer* **1986**, *27*, 1071.
(36) Burchard, W., personal communication.
(37) Brown, W. *Macromolecules* **1986**, *19*, 3006.
(38) Brown, W.; Štěpánek, P., in press..
(39) Amis, E. J.; Han, C. C.; Matsushita, Y. *Polymer* **1984**, *25*, 650.
(40) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 1567.
(41) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 7164.
(42) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 7174.
(43) Rendell, R. W.; Ngai, K. L.; McKenna, C. B. *Macromolecules* **1987**, *20*, 2250.
(44) Chang, T.; Yu, H. *Macromolecules* **1984**, *17*, 115.
(45) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636.
(46) Adam, M.; Delsanti, M. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, 713.
(47) Huber, K.; Bantle, S.; Burchard, W.; Fetters, L. J. *Macromolecules* **1986**, *19*, 1404.
(48) **Note Added in Proof**: Recalculation of the data at −40 °C for the middle mode by using multiangle analysis shows that it consists of two separable peaks, both of which correspond to K-independent structural relaxations. When shifted by (T/η_0), these peaks coincide with the middle and slow peaks found for the same polymer fraction in another θ system (PS/dioctyl phthalate, 22 °C).
(49) Livesey, A. K.; Licinio, P.; Delaye, M. *J. Chem. Phys.* **1986**, *84*, 113.
(50) Licinio, P.; Delaye, M.; Livesey, A. K.; Léger, L. *J. Phys. (Les Ulis, Fr.)* **1987**, *48*, 1217.
(51) Livesey, A. K.; Delaye, M.; Licinio, P.; Brochon, J.-C. *Faraday Discuss. Chem. Soc.* **1987**, *No. 83*.
(52) Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1983**, *44*, 35.

Noncooperative Relaxations

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ABSTRACT: Dynamic mechanical studies have revealed a large class of internal motions having activation entropies close to zero which appear to involve well-defined structural units acting in a noncooperative manner. Examples include rotations of methyl groups, certain side-group motions, and local-mode relaxations which are restricted to short polymethylene sequences. Other cases, including grain boundary relaxations in metals, are associated with crytalline phases.

Introduction

The relationship between the frequency and the temperature of a viscoelastic relaxation can be expressed as an Arrhenius equation:

$$f = Ae^{-E_a/RT} \tag{1}$$

An alternative relationship is derived from the theory of absolute reaction rates.

$$f = \frac{kT}{2\pi h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \tag{2}$$

The relationship between the Arrhenius activation energy, E_a, and the activation enthalpy, $\Delta H^\ddagger$, is

$$E_a = \Delta H^\ddagger + RT \tag{3}$$

From eq 2 and 3, it follows that

$$E_a = RT[1 + \ln (kT/2\pi hf)] + T\Delta S^\ddagger \tag{4}$$

If the activation entropy, $\Delta S^\ddagger$, is zero, the relationship between the activation energy and T', the temperature at which the frequency of the relaxation is 1 Hz, becomes

$$E_a = RT'[1 + \ln (kT'/2\pi h)] = RT'(\ln T' + 22.922) \tag{5}$$

If the energy difference between the potential minima is small, there can be an additional term of up to $RT' \ln 2$.[1] This is roughly equivalent to the width of the points

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Table I
β-Relaxation in Poly(methyl methacrylate)

	temp, °C			temp, °C	
freq, Hz	at tan δ_{max}	at E''_{max}	freq, Hz	at tan δ_{max}	at E''_{max}
0.033	6	-3	3	51	44
0.1	25	10	10		56
0.33		18	30		64
1.0	43	24			

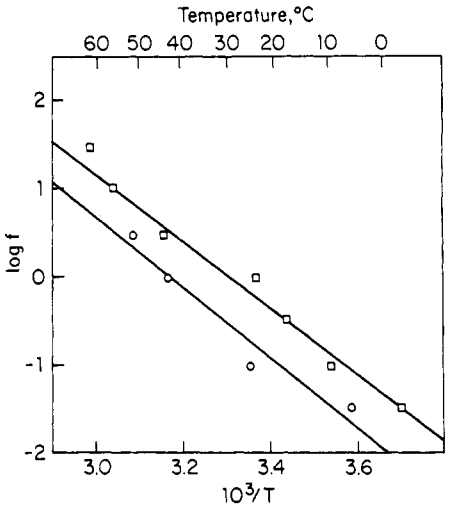

Figure 1. Arrhenius plot for the β-relaxation in poly(methyl methacrylate): (○) tan δ_{max}; (□) E''_{max}.

in Figures 2, 3, and 6 and is thus within the range of experimental uncertainty.[1]

We have found[2] that eq 5 pretty well defines a lower limit for the activation energies of viscoelastic relaxations. In earlier work,[2] relaxations having activation entropies close to zero were called simple relaxations, and those having large positive activation entropies were called complex relaxations. It is believed that large activation entropies and energies reflect cooperative effects among the moving segments. Glass transitions which frequently have apparent activation energies greater than the strength of a primary chemical bond are striking examples of these characteristics. Therefore, relaxations which have activation entropies close to zero will now be referred to as noncooperative relaxations. Relaxations attributed to motions of methyl groups are examples of this category.[2] Several other classes of noncooperative relaxations have now been identified.

Side Group Relaxations

The β-relaxations in acrylic and vinyl polymers are widely attributed to the local motions of ester side groups.[3] Recently, the methods of molecular mechanics have been applied to this phenomenon in poly(methyl methacrylate).[4,5]

We studied the β-relaxation in PMMA using the Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) at seven frequencies from 0.033 to 30 Hz. The temperatures of the maxima in tan δ and the loss modulus, E'', are given in Table I and presented in an Arrhenius plot in Figure 1. The activation energy and temperature at f = 1 Hz are 18.1 kcal/mol and 315 K for the data at tan δ_{max} and 17.2 kcal/mol and 302 K for the data at E''_{max}. Both of these conditions correspond to $\Delta S^{\ddagger} = 0$ within experimental uncertainty. Cowie and Ferguson[4] calculated energies in this range for rotation about the bond connecting the backbone to the carbonyl group provided that the adjacent ester side groups are allowed to undergo torsional oscillations of ±16° and the main-chain carbon

Table II
β-Relaxation in Poly(vinyl acetate)

	temp, °C			temp, °C	
freq, Hz	at tan δ_{max}	at E''_{max}	freq, Hz	at tan δ_{max}	at E''_{max}
0.33	-116	-116	10	-96	-97
1.0	-103	-107	30	-88	-91
3	-102	-99	90	-80	-79

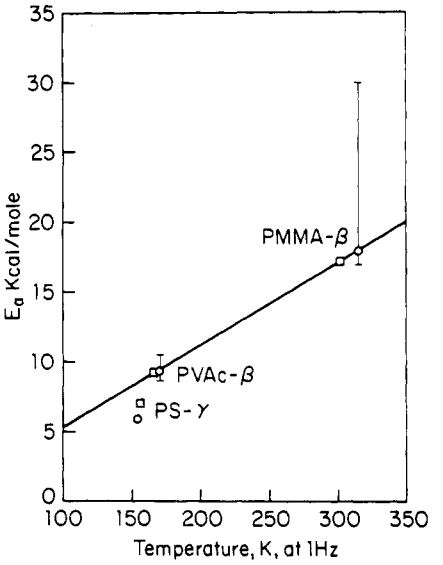

Figure 2. Side-group relaxations: (○) tan δ_{max}; (□) E''_{max}; line, $\Delta S^{\ddagger} = 0$; vertical bars, range of literature values.

and its attached methyl group are allowed to relax. The methyl group relaxation has been assigned to a loss peak occurring at a lower temperature.[2,3] Heijboer and coworkers[5] computed an energy of 16.5 kcal/mol for rotation about the main-chain carbonyl bond when appropriate constraints were applied to the main-chain torsion angles.

Data for the dependence of the β-relaxation in poly(vinyl acetate) on temperature and frequency are given in Table II. The activation energy of about 9.3 kcal/mol and a temperature of about 168 K at f = 1 Hz correspond to $\Delta S^{\ddagger} = 0$.

In polystyrene, the β-relaxation was observed at 52 °C (f = 1 Hz) with an activation energy of 38 kcal/mol. This relaxation clearly has cooperative character. The small, low-temperature γ-relaxation is more difficult to define. Data taken at 3–90 Hz indicate an activation energy of 7 kcal/mol and a temperature of 156 K at f = 1 Hz. An activation energy of 8.7 kcal/mol was expected for $\Delta S^{\ddagger} = 0$.

The situation for these side-group relaxations is summarized in Figure 2. Our data lie on or close to the line for noncooperative relaxations for which $\Delta S^{\ddagger}$ is zero. The range of literature values for the activation energies is indicated by vertical bars. The condition, $\Delta S^{\ddagger} = 0$, is close to the lower limits for the reported values. A rather wide range of values has been reported for the β-relaxation in PMMA. Our vlaues of 17–18 kcal/mol agree with those of McCrum and Morris,[6] Hoff and Reddish,[7] and Heijboer.[8]

The conclusion that the β-relaxations in PMMA and poly(vinyl acetate) involve noncooperative motions of the ester side groups is supported by the effect of absorbed solvents such as toluene and acetone. As shown in Table III, these additives cause the glass transition to shift to markedly lower temperatures, the typical effect of plasticizers. However, the temperatures and peak heights of the β-relaxations are unchanged even up to 6% additive. These observations are in line with dielectric studies by Mikhailov et al. on PMMA containing up to 25% dibutyl

Table III
Effect of Absorbed Solvents on the Temperatures of Relaxations Measured at 1 Hz

additive	glass temp, °C: at tan δ_{max}	glass temp, °C: at E''_{max}	temp of β-relaxtn, °C: at tan δ_{max}	temp of β-relaxtn, °C: at E''_{max}
		Poly(methyl methacrylate)		
none	122	108	23	23
0.30% toluene	90	88	29	25
0.87% toluene	84	78	22	20
1.37% toluene	71	66	22	18
3.21% toluene	54	51		11
1.06% acetone	83	82	30	16
2.03% acetone	85	76	25	19
4.35% acetone	49	43	29	22
			av 26 ± 4	19 ± 4
		Poly(vinyl acetate)		
none	56	49	−107	−107
2.29% toluene		19	−100	−107
4.42% toluene		15	−105	−105
1.34% acetone		18	−102	−102
2.29% acetone	17	16	−100	−100
6.24% acetone	15	8	−100	−100
			av −102 ± 3	−103 ± 3

phthalate.[9] In a study of mechanical properties, Heijboer[8] also concluded that plasticizing PMMA with dibutyl phthalate does not change the location of the β-relaxation. There was an increase in the maximum value of tan δ[10] but little effect on the loss modulus, which is proportional to the energy absorbed per cycle in an experiment using a defined strain amplitude.[3]

Local-Mode Polymethylene Relaxations

For many polymers, the local-mode relaxation has a large activation entropy.[2] However, for nylon 66, this quantity is much smaller than for polyethylene, poly(oxymethylene), or poly(tetrafluoroethylene). It is thought that the hydrogen bonds between amide groups tend to restrict these motions to a narrow range of polymethylene sequences. Long ago, Willbourn[11] observed that a loss peak similar to the γ-relaxation in polyethylene occurs in all polymers having sequences of four or more methylene units. We have examined a number of polymers having polymethylene sequences close to this lower limit.

The relationship between the activation energy and the temperature at $f = 1$ Hz for the polymethylene local-mode relaxation in various polymers is shown in Figure 3. The distance of a point above the line corresponding to $\Delta S^* = 0$ is equal to $T\Delta S^*$. While the activation entropy for the γ-relaxation in dry nylon 66 is much lower than in polyethylene, it becomes essentially zero in wet nylon. The height of the loss peak also decreases and almost disappears as water is absorbed, and the modulus at low temperatures is increased.[12] These effects are attributed to the formation of mechanically stable bridges between amide groups through water molecules.[13] This would limit the local-mode motions to the sequences of four or six methylene units in the acid and diamine moieties, respectively. In nylon 6I, the polyamide derived from hexamethylene diamine and isophthalic acid, the acid moiety is rigid, and ΔS^* for the γ-relaxation is close to zero even in the dry state.

At a frequency of 1 Hz, the dynamic mechanical properties of poly(butylene terephthalate) are dominated by the α-relaxation at 57 °C and the β-relaxation at −70 °C, which have activation energies of 152 and 26 kcal/mol, respectively. On the low-temperature side of the β-peak, there is a shoulder which we attribute to a polymethylene relaxation. A master curve obtained by shifting tan δ data along the log-frequency axis by using a reference temperature of −100 °C is presented in Figure 4. The points

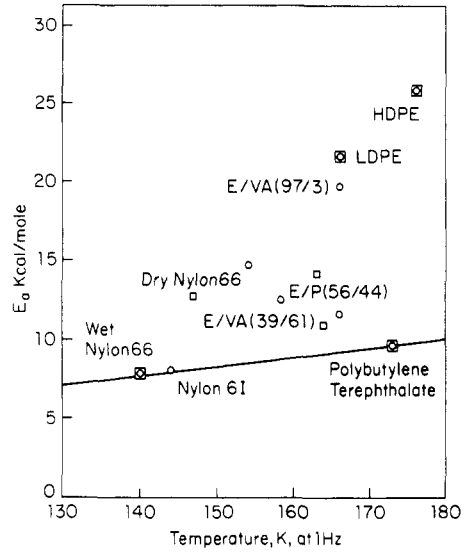

Figure 3. Activation energies of local-mode relaxations: (○) tan δ_{max}; (□) E''_{max}; line, $\Delta S^* = 0$.

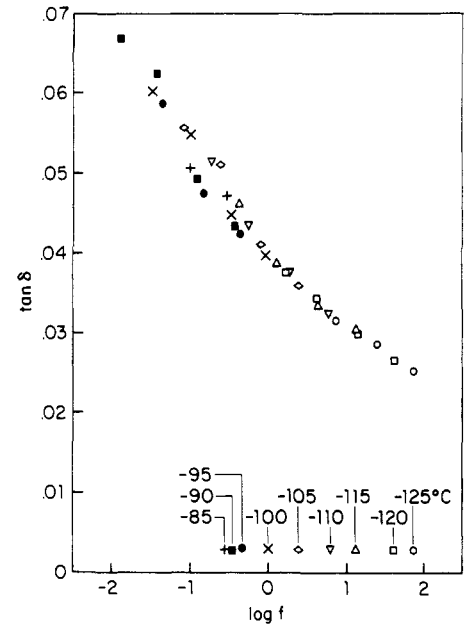

Figure 4. Master curve for the polymethylene relaxation in poly(butylene terephthalate).

along the abscissa indicate the position of $\log f = 0$ in the original data. An Arrhenius plot of these shift factors is shown in Figure 5. The slope for the tan δ data taken at temperatures from −120 to −95 °C corresponds to an activation energy of 9.6 kcal/mol and an activation entropy close to zero at the reference temperature.

Some addition polymers having relatively short polymethylene sequences were also examined. E/VA (39/61) is a copolymer of vinyl acetate with 17% ethylene by weight (39 mol%). More than half of the ethylene units are in sequences of one or two. As shown in Figure 3, the γ-relaxation in this copolymer has a small but finite activation entropy. However, in E/VA (97/3), an ethylene/vinyl acetate copolymer containing 97 mol% ethylene, the activation entropy was almost as large as in low-density polyethylene. We also studied a copolymer of propylene with 56 mol % ethylene. In this case, the activation entropy for the γ-relaxation was larger than in E/VA (39/61) but smaller than in polymers containing higher levels of ethylene.

All of the data used to prepare Figure 3 were obtained in a similar manner by using the Polymer Laboratories

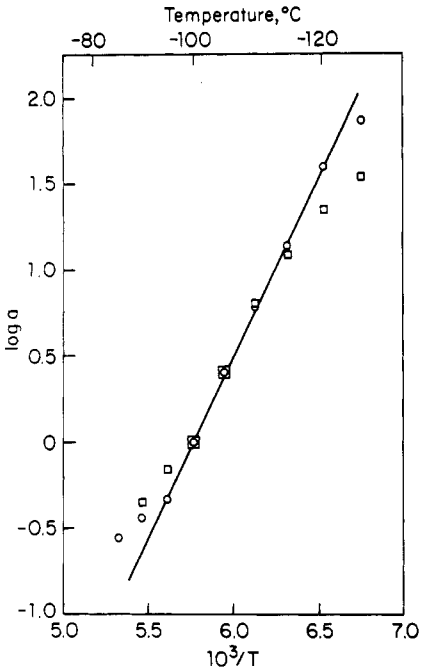

Figure 5. Arrhenius plot for the frequency–temperature shift factors for the polymethylene relaxation in poly(butylene terephthalate): (○) tan δ_{max}; □ E''_{max}.

DMTA. The activation energies for the γ-relaxation in polyethylene are larger than those reported elsewhere.[2,3] We suspect that these differences reflect varying degrees of cooperative character which result from differences in sample history.

Helfand has concluded that the γ-relaxation involves the transformation of a TTT sequence to a GTG' sequence.[14,15] Related mechanisms have been offered by Boyer,[16] Schatzki,[17] and Boyd and Breitling.[18] In polymers containing sequences of only four to six methylene units, these motions must occur independently of one another. With longer sequences, all sorts of cooperative motions are possible. Since the γ-relaxation in nylon 66 is dielectrically active, there must be some motion of the amide groups. There is, apparently, a limited degree of cooperation in the motion of the polymethylene sequences on both sides of an amide, unless the amides are immobilized by the formation of mechanically stable bridges through water molecules bonded to the carbonyl oxygens. The magnitude of the activation entropy is governed by the length of the polymethylene sequences.

Crystalline Relaxations

A few relaxations associated with motions in crystals have been found for which the activation entropy is close to zero. The first of these is the γ_c-relaxation in poly(chlorotrifluoroethylene).[2,19] This motion is associated with short-chain segments in the crystals. A possibly analagous process is the γ_{III}-relaxation in polyethylene.[2,20,21] More recently, it has been found that the α-relaxation in polyoxymethylene also has an activation entropy near zero.[22] This important process occurs at 130 °C at a frequency of 1 Hz and governs much of the viscoelastic behavior at room temperature.

The occurrence of noncooperative crystalline relaxations is not limited to polymers. According to Kê,[23] polycrystalline aluminum has a relaxation which is not present in a single crystal. A peak in tan δ was reported at 285 °C at a frequency near 1 Hz. The activation energy of 32 kcal/mol agrees with the relationship for $\Delta S^* = 0$. Data

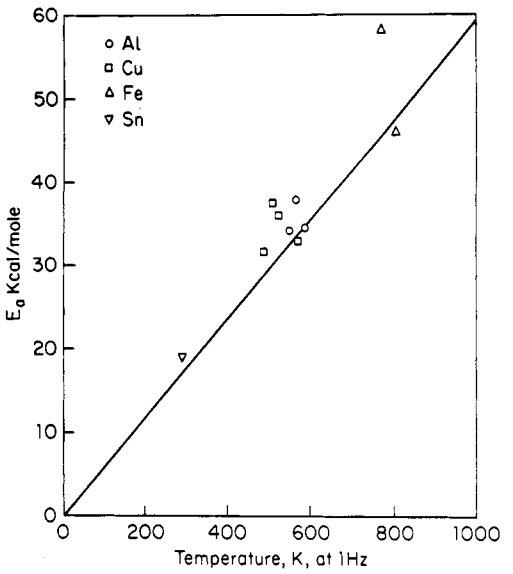

Figure 6. Activation energies for grain boundary relaxations in metals: line, $\Delta S^* = 0$.

from the literature[24] for the temperatures and activation energies for grain boundary relaxations in several metals are plotted in Figure 6. As is the case with several other kinds of relaxations, the lowest reported values for the activation energies correspond to activation entropies close to zero. Some metals have additional relaxations at higher temperatures with large positive activation entropies.

Conclusions

Noncooperative relaxations, characterized by activation entropies close to zero, are thought to be the elemental components of internal motions. The class includes many kinds of moving units. At least in some cases, a fairly detailed mechanistic understanding is possible.

Registry No. PMMA, 9011-14-7; PVAc, 9003-20-7; PS, 9003-53-6; PE, 9002-88-4; (VA)(E) (copolymer), 24937-78-8; (P)(E) (copolymer), 9010-79-1; nylon 66 (SRU), 32131-17-2; nylon 6I (SRU), 25668-34-2; nylon 6I (copolymer), 25722-07-0; Al, 7429-90-5; Cu, 7440-50-8; Fe, 7439-89-6; Sn, 7440-31-5; poly(butylene terephthalate) (SRU), 24968-12-5; poly(butylene terephthalate) (copolymer), 26062-94-2.

References and Notes

(1) Hoffman, J. D.; Pfeiffer, H. G. *J. Chem. Phys.* **1954**, *22*, 132.
(2) Starkweather, H. W. *Macromolecules* **1981**, *14*, 1277.
(3) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(4) Cowie, J. M. G.; Ferguson, R. *Polymer* **1987**, *28*, 503.
(5) Heijboer, J.; Baas, J. M. A.; van de Graaf, B.; Hoefnagel, M. A. *Polymer* **1987**, *28*, 509.
(6) McCrum, N. G.; Morris, E. L. *Proc. R. Soc. London, A* **1964**, *281*, 258.
(7) Hoff, E. A. W.; Reddish, W. *J. Polym. Sci.* **1954**, *13*, 565.
(8) Heijboer, J. *Kolloid Z.* **1956**, *134*, 149; **1956**, *148*, 36.
(9) Mikhailov, G. P.; Borisova, T. I.; Dmitrochenko, D. A. *Sov. Phys.—Tech. Phys. (Engl. Transl.)* **1956**, *1*, 1857.
(10) Heijboer, J. In *Molecular Basis of Transitions and Relaxations*; Meier, D. J., Ed.; Gordon and Breach: New York, 1978; pp 75–102.
(11) Willbourn, A. H. *Trans. Faraday Soc.* **1958**, *54*, 717.
(12) Ikeda, R. M.; Starkweather, H. W. *Polym. Eng. Sci.* **1980**, *20*, 320.
(13) Starkweather, H. W. In *Water in Polymers*; Edwards, S. P., Ed.; ACS Symposium Series 127; American Chemical Society: Washington, DC, 1980; p 433.
(14) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(15) Helfand, E. *Science (Washington, D.C.)* **1984**, *226*, 647.

(16) Boyer, R. F. *Rubber Chem. Technol.* **1963**, *34*, 1303.
(17) Schatzki, T. F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1965**, *6*, 646.
(18) Boyd, R. H.; Breitling, S. M. *Macromolecules* **1974**, *7*, 855.
(19) Hoffman, J. D.; Williams, G.; Passaglia, E. *J. Polym. Sci., Part C* **1966**, *14*, 173.
(20) Illers, K. H. *Kolloid Z. Z. Polym.* **1969**, *231*, 662.
(21) Arridge, R. G.; Parham, P. J. *Polymer* **1978**, *19*, 603.
(22) Starkweather, H. W. *Macromolecules* **1986**, *19*, 2538.
(23) Kê, T. *Phys. Rev.* **1947**, *71*, 533; **1947**, *72*, 41.
(24) Nowick, A. S.; Berry, B. S. *Anelastic Relaxation in Crystalline Solids*; Academic: New York, 1972.

Phase Contrast Matching in Lamellar Structures Composed of Mixtures of Labeled and Unlabeled Block Copolymer for Small-Angle Neutron Scattering

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ABSTRACT: To extract the single-chain scattering function of polystyrene block chain in lamellar structures of styrene–2-vinylpyridine diblock copolymers, the method of "phase contrast matching" was studied for small-angle neutron scattering from blends of the deuterium-labeled and unlabeled block copolymers. The phase contrast matching is successfully applied for the samples with the lowest molecular weights (3.4×10^4 for the labeled portions) but not for the samples with the higher molecular weights (9.2 and 16.2×10^4). It is concluded that the mismatching may be caused by concentration fluctuation in the mixture of hydrogenated and deuteriated polystyrenes in domains, as well as by nonuniform distribution of deuteriated species along the direction perpendicular to the lamellae due to the difference in lengths of the labeled and unlabeled blocks.

Introduction

The conformation of a single polymer chain in bulk can be determined by measuring small-angle neutron scattering (SANS) from a random mixture of deuterium-labeled and unlabeled polymers with the same chain length at any mixing ratio. The same method is applicable for determining the conformation of a block chain of diblock copolymer even in a microdomain structure, if strong diffraction intensities from the microdomain structure could be eliminated. Three methods were employed to eliminate the diffraction. In the first method a single-chain scattering function is obtained as the difference between the coherent scatterings from a blend of labeled and unlabeled block copolymers and its corresponding unlabeled block copolymer. This method is straightforward, but it is difficult to obtain reliable data for a single-chain conformation since the diffraction intensity due to the domain structure is much higher than the single-chain scattering and also identical domain structures are required for the both specimens in order to eliminate the scattering due to the domain structure. Richards and Thomason[2] employed this method to study styrene block dimensions in the spherical domain of styrene–isoprene block copolymer. Unfortunately, the chain lengths of the parent and deuteriated samples were not the same and the measurements were carried out at a low content of deuteriated sample.

The second method involves the utilization of anisotropy of a microdomain structure. If the plane of lamellar surface could be aligned perpendicular to the incident neutron beam, the diffraction due to the lamellar structure would not be observed and only a single-chain scattering from labeled and unlabeled blocks could be obtained. Hadzioannou et al.[3] and Hasegawa et al.[4] investigated conformations of polystyrene block in a lamellar structure of styrene–isoprene copolymers by this method. Since the orientation of lamellae was not perfect in their experiments, Hadziioannou et al.[3] obtained a single-chain scattering at a particular azimuthal angle where the diffraction was not observed, while Hasegawa et al.[4] subtracted the contribution of diffraction with the use of the scattering data from the parent block copolymer.

In the third method, the diffraction is eliminated by matching the average scattering lengths between the two phases ("phase contrast matching") due to random mixing of labeled and unlabeled block chains. This method was first proposed for polymer blends by Jahshan and Summerfield[5] and subsequently extended to block copolymers by Koberstein.[6] According to their theory the coherent scattering intensity from a single chain in a microdomain structure of blend of labeled and unlabeled A–B diblock copolymers with the same chain length can be written as

$$I(q) = [(I_L - I_{B,L}) - R(I_U - I_{B,U})] \quad (1)$$

where I_L and I_U are the total scattering intensities from the labeled and unlabeled polymers, respectively, and the subscript B refers to the background mainly composed of incoherent scattering. In eq 1 the first term of the right-hand side is the total coherent scattering from the microdomain structure containing labeled block chains, and the second term is the contribution from the microdomain structure itself. R in the second term is the magnitude of contrast between two phases such as

$$R = [\beta_B - x\beta_{AD} - (1 - x)\beta_{AH}]^2/(\beta_B - \beta_{AH})^2 \quad (2)$$

where β_B, β_{AH}, and β_{AD} are the coherent scattering length densities of block B and hydrogenated and deuteriated

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