Polymer Journal

Special Issues –International Symposium on Polymer Crystallization 2007–

On the Stability of the Nematic Order Observed During the Cold-crystallization of PET

By Akihiro ABE,[1,*] Hidemine FURUYA,[2] Toshihiro HIEJIMA,[1] and Tsuyoshi NISHIYAMA[1]

The rotational isomeric state analysis of poly(ethylene terephthalate) (PET) was carried out by using parameters adjusted so as to reproduce the experimental results of ^{1}H NMR and dipole moment measurements on ethylene glycol dibenzoate. The central OC-CO bond of the ethyleneglycol unit prefers to be in the gauche form at lower temperatures, suggesting that the PET chains should contain many kink conformations in the amorphous state. In the following part, the nematic conformation of the same C-C bond was studied by preparing a model compound which is capable of forming an enantiotropic nematic liquid crystalline (LC) phase. IR studies indicate that the trans fraction of the C-C bond increases from ∼15% in the isotropic liquid to ∼50% in the nematic LC state at the phase boundary. For this drastic change in the conformation at the transition, the C-C bond should be required to pay certain entropy penalty. These results are however compatible with the recent observations by SAXS and DPLS that the formation of nematic LC-like domains proceeds prior to the evolution of primary crystal nucleation during the cold-crystallization of PET. The PET chain is known to take the planar all-trans conformation in the crystalline state. Finally a possible mechanism leading to the nematic order in the amorphous PET is presented. Growth of the nematic LC-like domains in the amorphous phase may lead to a spinodal microphase separation, as suggested by Kaji *et al.*

KEY WORDS: Poly(ethylene terephthalate) / RIS Analysis / Nematic Conformation / Cold-crystallization / Spinodal Decomposition /

The spatial configurations and intermolecular packing of polymer chains in the amorphous state are largely affected by the rotational characteristics of the constituent bonds. Upon crystallization, the polymer chains are required to uniformly take an ordered configuration to attain a dense packing. In most polymers, the crystalline form is found to coincide with one of the lowest energy arrangements of the free chain.[1–3] The poly(ethylene terephthalate) (PET) chain is an exception, in which the chain goes through a large transformation to a high-energy conformation during the crystallization process.[1,4]

Recently, substantial number of observations have been accumulated in favor of the "mesomorphic phase" model as a mechanism of the cold-crystallization of polymers.[5–10] Kaji *et al.*[6] have proposed a spinodal decomposition (SD)-type microphase separation triggered by the density (orientation) fluctuation due to severe steric conflicts (excluded volume) among stiff segments. In these studies, one of the most frequently used samples is PET. As well-known, the -OC-CO- moiety of this polymer chain strongly prefers the gauche state, either g^+ or g^-, in the unconstrained free state: *i.e.*, the fraction f_g increases with decreasing temperature.[11,12] The gauche form must be highly populated in a quenched amorphous state. The afore-mentioned observation that the formation of mesomorphic domains proceeds prior to the primary crystal nucleation may be understandable if, and only if, the ethyleneglycol (EG) residue -OCH$_2$CH$_2$O- undergoes a transformation to the planar conformation at the annealing temperature slightly above T_g. In

contrast to most conventional polymer chains, however, the extended trans conformation is a high-energy form of the PET chain. As long as chains are allowed to orient randomly in space, the individual polymer chains would not be willing to pay this penalty. Only when the molecules can attain higher stability by forming a nematic liquid crystal (LC) domain, they may cooperatively transform from the coil to an ordered form.

In this article, we would like to first discuss the conformational characteristics intrinsic to the PET chain, and then briefly mention the results of our experimental studies on the nematic conformation of a dimer (twin) compound carrying an EG spacer, which is capable of forming a nematic mosophase between the isotropic liquid and the crystal. Finally a possible mechanism of forming a nematic LC-like order during the cold-crystallization from the disordered amorphous PET will be presented.

SPATIAL CONFIGURATION OF THE PET CHAIN IN THE AMORPHOUS STATE DELINEATED ACCORDING TO THE RIS MODEL

The RIS calculation of the PET chain has been performed according to the conventional method.[11,12] The chemical structure of the backbone chain is schematically shown in Figure 1. The conformational statistical weight parameters appended to the individual bonds were those estimated by the ^{1}H NMR and dipole moment analysis on ethylene glycol

[1]Department of Applied Chemistry, Tokyo Polytechnic University, 1583 Iiyama, Atsugi 243-0297, Japan
[2]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-H-128 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
*To whom correspondence should be addressed (Tel/Fax: +81-46-242-9536, E-mail: aabe@chem.t-kougei.ac.jp).
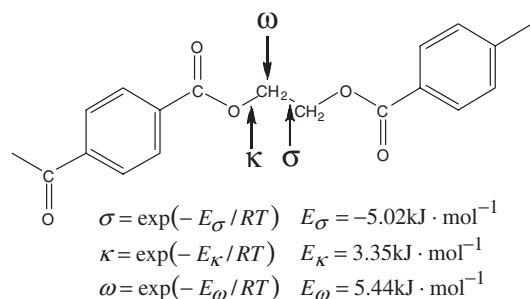
$$\sigma = \exp(-E_\sigma / RT) \quad E_\sigma = -5.02\,\text{kJ}\cdot\text{mol}^{-1}$$
$$\kappa = \exp(-E_\kappa / RT) \quad E_\kappa = 3.35\,\text{kJ}\cdot\text{mol}^{-1}$$
$$\omega = \exp(-E_\omega / RT) \quad E_\omega = 5.44\,\text{kJ}\cdot\text{mol}^{-1}$$

Figure 1. The chemical structure of PET and the definition of RIS parameters for the bond rotation.

Table I. Geometrical Parameters used for the RIS calculation

Bond angle	Angle/deg.	Torsion angle	Angle/deg.
$\angle C^{ar}CO$	113.0	CO–CC	±104
$\angle COC$	115.7	OC–CO	±118
$\angle OCC$	115.0		
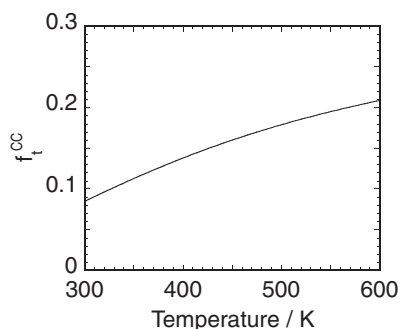
Figure 2. Temperature dependence of the trans fraction f_t^{CC} around the OC-CO bond.

Figure 3. Regular (one-dimensional) arrangements of the PET chain with the lowest conformational energy.
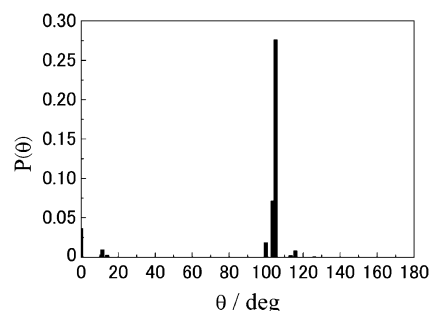
Figure 4. Conformer population $P(\theta)$ for the disorientation angle θ, calculated for the temperature of 25 °C.

dibenzoate (EGDB) in benzene solution.[13] The geometry of the ester group is taken to be cis. The arrangement of the ester groups situated on both sides of a phenylene group may be either cis or trans across the aromatic ring: statistical weight γ used to differentiate these two configurations is usually set equal to unity in the random coil state. Geometrical parameters of the chain (Table I) were adopted from the crystal structure of EGDB reported by Perez *et al.*[14] The PET chain includes three rotatable bonds in the EG unit. To adopt a nematic alignment, the orientational correlation of the neighboring phenylene units is crucially important. To avoid the occurrence of a kink conformation, the OC-CO bond preferably remains in the planar trans arrangement. As is shown in a large negative value of E_σ, the OC-CO bond strongly prefers to take a gauche form, either g⁺ or g⁻, in the free state. Thermal variation of the trans fraction f_t^{CC} ($= 1 - f_g^{CC}$) around the OC-CO bond is shown in Figure 2. The estimate is found to be in good accord with those previously reported by Schneider *et al.*,[15] who have carried out extensive studies on EGDB in solution by a combined use of NMR, Raman and IR absorption. The energy difference between the two rotational states is calculated to be
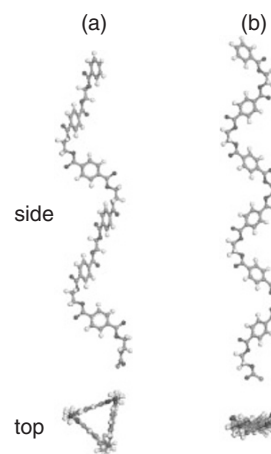
$4.2\,\text{kJ}\,\text{mol}^{-1}$ in agreement with the experimental deduction by the temperature dependence of IR absorption peaks (3.6–4.2 $\text{kJ}\,\text{mol}^{-1}$).[15]

As temperature lowers, f_t tends to decrease while f_g increases. It is important to note that the rotation around the central OC-CO bond most effectively determines the relative orientation of the terminal phenylene groups. Due to the bond angle restriction, the effect arising from the internal rotation around the bond lying parallel to the phenylene axis (*e.g.*, O-C, C-O) is much smaller.

One-dimensional arrays of the PET chain may also be constructed by adopting a regular repetition of either -(tg⁺t)- or -(tg⁻t)-, or an alternation of -(tg⁺t)- and -(tg⁻t)- arrangements. While the former leads to a helical conformation of a large diameter (8.8 Å) (Figure 3a), the latter yields a planar zigzag arrangement with a step spanning a repeating unit of the chain (7.0 Å top view) (Figure 3b). These configurations are energetically most stable, but may not be too efficient for a dense packing. In fact, the PET chain crystallizes in the planar (trans) conformation.

Figure 4 indicates the distribution of the disorientation angle between the neighboring phenylene axis joined by an EG unit. The PET chain should comprise many kink conformations ($\theta = 100–110°$) in the randomly packed amorphous state. The
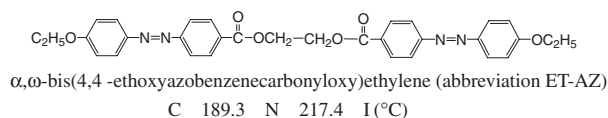
gauche preference of the OC-CO bond is largely responsible for such disordered arrangements. The conformational entropy change ΔS^{conf} on going from the crystalline to random state may be estimated on the basis of the conformer distribution shown in Figure 4. The value of $\Delta S^{conf} = 37.0 \, J \, mol^{-1} \, K^{-1}$ thus obtained corresponds to 60–75% of those ($(\Delta S_m)_P$) found for the repeating unit -$C(O)C_6H_4C(O)OCH_2CH_2O$- (PET) from the measurements on EGDB ($64 \, J \, mol^{-1} \, K^{-1}$)[13] and PET ($49 \, J \, mol^{-1} \, K^{-1}$).[16] *PVT* studies on conventional chain molecules often reveal that 30–50% of the entropy of fusion $(\Delta S_m)_P$ determined under the isobaric condition arises from the volume change ΔS_V at the phase transition.[2,3,17,18]

$$(\Delta S_m)_P = (\Delta S_m)_V + \Delta S_V \tag{1}$$

The conformational entropy ΔS^{conf} accounts for the major part of the constant-volume transition entropy $(\Delta S_m)_V$.

ELUCIDATION OF THE NEMATIC CONFIGURATION OF THE OC-CO MOIETY USING A MODEL COMPOUND

In order to examine the nematic form of the EG sequence, we have prepared a dimer compound carrying mesogenic units on both terminals by a conventional technique:[19,20]

C_2H_5O—⟨ ⟩—N=N—⟨ ⟩—$\overset{O}{\overset{\|}{C}}$—$OCH_2$—$CH_2O$—$\overset{O}{\overset{\|}{C}}$—⟨ ⟩—N=N—⟨ ⟩—$OC_2H_5$

α,ω-bis(4,4′-ethoxyazobenzenecarbonyloxy)ethylene (abbreviation ET-AZ)

C   189.3   N   217.4   I (°C)

The DSC data observed on heating at a rate of $10 \, °C/min$ are given to the chemical structure. On cooling, crystallization took place at $157.3 \, °C$. The nematic texture was observed under a polarizing microscope on both heating and cooling process.

The profiles of the IR absorption spectra obtained at various temperatures are shown in Figure 5. According to Manley *et al.*[21] and Schneider *et al.*,[15,22] the two peaks observed around 1340 and $1370 \, cm^{-1}$ may be respectively due to the CH_2
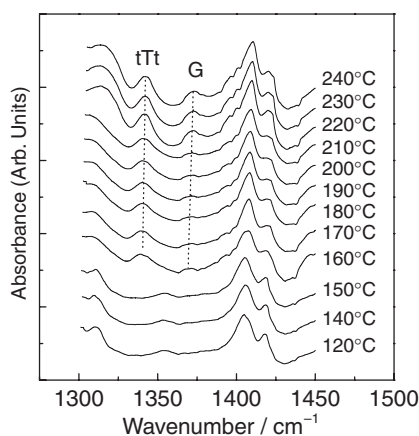

Figure 5. IR spectra of ET-AZ for the I ~ N region observed on cooling: peak assignments were made after Schneider *et al.*'s work.[15,22]
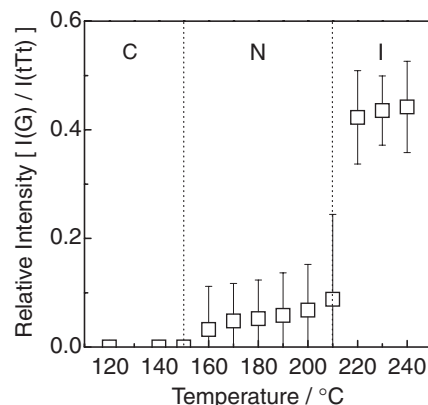

Figure 6. Temperature dependence of the relative intensity of IR peaks (I_g/I_t), taken from Figure 5.

wagging mode in the tTt and G form of EGDB, a model compound of PET, in liquid. Following their assignment, the relative intensities of the gauche (I_g) at $1370 \, cm^{-1}$ and trans (I_t) absorption at $1339 \, cm^{-1}$ are estimated by a deconvolution and curve-fitting, and the results are plotted against temperature in Figure 6. From the other evidences,[23] ET-AZ is known to crystallize in the ttt conformation: the IR peaks observed at $1351 \, cm^{-1}$ may be due to the crystalline arrangement (see Figure 5). Since the absorption coefficients of these peaks are not known, the ratio I_t/I_g should be taken as a measure proportional to the relative amount of the gauche and trans conformers around the OC-CO bond. An abrupt change of the ratio took place at the NI phase boundary (see Figure 6). Since the NI transition temperature is close to the upper limit of the apparatus, a more quantitative analysis by NMR could not be carried out. Adopting the energy difference $4.2 \, kJ \, mol^{-1}$,[13,15] $f_t^{CC} = {\sim}15\%$ in the high-temperature liquid state (${\sim}230 \, °C$). The f_t^{CC} in the nematic LC state becomes about ${\sim}50\%$ (*i.e.*, 25% each for g^+ and g^-) in proportion, suggesting that the OC-CO bond of ET-AZ favors the trans arrangement in the nematic environment. A sudden change of the rotational preference is a characteristic of the EG unit. Essentially the same behavior has been observed for longer oxyethylene spacers such as -$(OCH_2CH_2)_xO$- (x = 2–9) joined with appropriate mesogenic units *via* the ether linkage.[24,25] 1,2-Diphenyloxyethane $C_6H_5OCH_2CH_2OC_6H_5$, a nonmesogenic compound, exhibits a similar conformational transition when dissolved in a nematic solvent.[26]

According to Deguire *et al.*,[27] EGDB carrying a substituent (X) at the para-position forms either a trans (X = H, OCH_3, CN) or gauche crystal (X = CH_3, Cl) depending on the chemical nature of X. In the former group, the transformation to the trans form should be directed on the surface of the crystalline nucleus. In contrast, the most stable conformation in the liquid state is preserved in the latter examples. When the crystallization proceeds through an interstitial nematic state, as shown in this study, the transformation to the trans conformation cooperatively takes place on crossing the NI phase border.

GENERAL REQUIREMENT FOR THE FORMATION OF THERMOTROPIC NEMATIC LCS AND THE ADAPTABILITY TO THE PET CHAIN

The van der Waals attractive potential effective in the nematic mesophase may be expressed in a generalized form:[25,28,29]

$$E = -\eta/V = -(\eta_{iso} + \eta_{aniso}(s^2))/V \tag{2}$$

where η represents the strength of the interaction comprising the isotropic and anisotropic contributions, V is the volume, and s the orientational order parameter of the mosogenic cores. The volume dependence $(1/V^2)$ of the Maier-Saupe potential has been modified in consideration of the mean-field expression of the pairwise interaction.[30–32] In order to optimize the anisotropic interactions $(\eta_{aniso}(s^2))$ in the mesophase, the cooperative bond rotation of the EG segments $-OCH_2\text{-}CH_2O$- is inevitable, accordingly the C-C bond being required to pay certain entropy penalty. A recent analysis of mainchain liquid crystals[25,28,29] suggests that (1) flexible segments (spacer) cooperatively participate in the anisotropic attractive interaction by adjusting relative orientation of hard cores, (2) the mitigation of the excessive repulsive interactions may lead to an increase of the volume fraction of unoccupied sites (free volume), and (3) as explicitly indicated by the orientational order parameter of the mesogenic cores, incorporation of the anisotropic interactions $\eta_{aniso}(s^2)$ causes substantial enhancement of the thermal expansion coefficient α in the nematic state.[29] As known from various thermodynamic theories of polymer liquids, α is closely related to the free volume of the liquid.[33,34]

The anisotropy of the terephthalate group may be too weak to develop liquid crystallinity under the ordinary condition. Similar to the pressure-induced liquid crystallinity of *p*-ethoxybenzoic acid,[35] however, the terephthalate core may perform the role under a highly sterically repulsive environment such as an amorphous packing at lower temperature. In effect, the EG segment must cooperatively rotate to adjust relative orientation of hard cores along the backbone chain. The entropy penalty of the flexible chain segment may be partly compensated by the increase of the free volume.[33,34] The chain segment may not be directly involved in the anisotropic attractive interactions, but indirect effect on the anisotropic interaction is not clearly understood. In any rate, the growth of the nematic order in the amorphous phase should lead to a SD-type microphase separation, which can be observed by SAXS and other related methods.

CONCLUDING REMARKS

In the above, we have presented a possible, but somewhat hypothetical in part, scheme leading to a nematic order in the amorphous PET. The point we wish to emphasize is the importance of the cooperative process involving both inter- and intramolecular aspects. For the PET chain, it is improbable to assume that the stiffening of a single chain at lower temperatures is the primary cause of the phenomenon.[36,37] Finally it should be noted that the formation of the nematic LC-like domain may not immediately imply any plausible pathway to get into the crystalline state. In this respect, Grebowicz and Wunderlich's work[38] on the cold-crystallization of a LC-forming polymer, poly(oxy-2,2′-dimethylazoxybenzene-4,4′-diyloxydodecanedioyl), is suggestive.[10] They have reported that the crystallization from the mesophase occurs by nucleation, followed by growth at considerable supercooling.

Kaji *et al.*[3] have postulated an essentially the same mechanism for the cold-crystallization of other polymers such as *iso*- and *syndiotactic* polystyrenes (PS).[6] The conformational characteristics of these polymers are quite different from PET.[11,12] Due to the articulated bulky side groups, readjustment of the orientation along the backbone is far more complicated in the PS system. These polymers do not carry any polarizable rigid groups lying along the main chain. Under these circumstances, the conformational change observed during the annealing process may not give rise to a nematic LC-like domain formation. Further elaboration is required as to whether the cold-crystallization of these polymers really proceeds through the same mechanism as that observed in PET.[8]

REFERENCES

1. H. Tadokoro, "Structure of Crystalline Polymers," John Wiley & Sons, New York, 1979.
2. L. Mandelkern, "Crystallization of Polymers," McGraw Hill, New York, 1964, Chap. 5.
3. L. Mandelkern, "Crystallization of Polymers," Cambridge University Press, Cambridge, 2002, vol. 1, Chap. 6.
4. R. de P. Daubeny, C. W. Bunn, and C. J. Brown, *Proc. R. Soc.*, **226**, 531 (1954).
5. M. Imai, K. Mori, T. Mizukami, K. Kaji, and T. Kanaya, *Polymer*, **33**, 4451 (1992).
6. K. Kaji, K. Nishida, T. Kanaya, G. Matsuba, T. Konishi, and M. Imai, *Adv. Polym. Sci.*, **191**, 187 (2005).
7. G. R. Strobl, "The Physics of Polymers," 2nd ed, Springer, Berlin, 1997, p 173.
8. M. Grasruck and G. Strobl, *Macromolecules*, **36**, 86–91 (2003).
9. T. Xu, Y. Bin, Y. Nakagaki, and M. Matsuo, *Macromolecules*, **37**, 6985 (2004).
10. B. Wunderlich, *J. Appl. Polym. Sci.*, **105**, 49 (2007).
11. P. J. Flory, "Statistical Mechanics of Chain Molecules," John Wiley & Sons, New York, 1969.
12. W. L. Mattice and U. W. Suter, "Conformational Theory of Large Molecules: The Rotational Isomeric State Model in Macromolecular Systems," John Wiley & Sons, New York, 1994.
13. H. Furuya, unpublished data.

14. S. Perez and F. Brisse, *Acta Crystallogr.*, **B32**, 470 (1976).
15. B. Schneider, P. Sedláček, J. Štotr, D. Doskočilová, and J. Lövy, *Collect. Czech. Chem. Commun.*, **46**, 1913 (1981).
16. A. Mehta, U. Gaur, and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 289 (1978).
17. A. Würflinger, *Colloid. Polym. Sci.*, **262**, 115 (1984).
18. A. Abe, H. Furuya, Z. Zhou, T. Hiejima, and Y. Kobayashi, *Adv. Polym. Sci.*, **181**, 121 (2005).
19. T. Nishiyama, Master Thesis, Tokyo Institute of Polytechnics, 1997.
20. T. Hiejima, T. Nishiyama, A. Abe, presented at International Symposium on Polymer Crystallization (ISPC-07), Mishima, Japan, September 22–24, 2007.
21. T. R. Manley and D. A. Williams, *Polymer*, **10**, 339 (1969).
22. J. Štokr, B. Schneider, D. Doskocilová, J. Lövy, and P. Sedláček, *Polymer*, **23**, 714 (1982).
23. T. Hiejima, unpublished work.
24. H. Furuya, H. Iwanaga, T. Nakajima, and A. Abe, *Macromol. Symp.*, **192**, 239 (2003).
25. A. Abe, T. Hiejima, Y. Kobayashi, Z. Zhou, and C. Nakafuku, *Macromolecules*, **40**, 1746 (2007).
26. A. Abe, E. Iizumi, and N. Kimura, *Liq. Cryst.*, **16**, 655 (1994).
27. S. Deguire and F. Brisse, *Can. J. Chem.*, **66**, 2545 (1988).
28. A. Abe, Z. Zhou, and H. Furuya, *Polymer*, **46**, 4368 (2005).
29. A. Abe, presented at ISPC-07, Mishima, Japan, September 22–24,
2007. The values of the thermal expansion coefficient at the NI transition point were estimated by extrapolation from the stable isotropic state (α_I) as well as the nematic region (α_N) for various LC samples ranging from the monomer to polymers. The ratios α_N/α_I were found to exceed unity in all cases examined. These results suggest that the entropy penalty of the flexible spacer may be partly compensated by the increase of the free volume.
30. R. L. Scott and J. H. Hildebrand, "Regular Solutions," Prentice-Hall, New Jersey, 1962.
31. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **39**, 173 (1977).
32. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 311 (1979).
33. a) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).
b) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3515 (1964).
34. R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
35. S. Chandrasekhar, "Liquid Crystals," 2nd ed, Cambridge University Press, Cambridge, 1992, p 29.
36. M. Doi and S. F. Edwards, "The theory of Poymer Dynamics," Oxford University Press, Oxford, 1986.
37. T. Shimada, M. Doi, and K. Okano, *J. Chem. Phys.*, **88**, 7181 (1988).
38. J. Grebowicz and B. Wunderlich, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 141 (1983).