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On the Mesophasic Behavior of Rodlike Polymers with Flexible Side Chains. Theory and Comparison with Experiments

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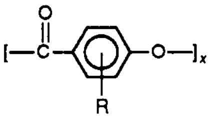
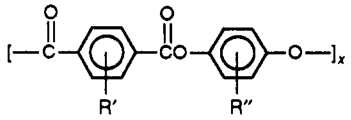
ABSTRACT: A statistical-thermodynamical lattice treatment of systems of chain molecules, previously developed to investigate the nematic/isotropic phase transitions of polymers with rigid and flexible parts alternating along the main chain, has been modified to study the mesophasic behavior of the title polymers. Two series of derivatives of poly(1,4-phenylene terephthalate) and of poly(1,4-oxybenzoyl), with alkyl groups of various lengths attached to the aromatic rings, have been modeled as proper sequences of isodiametric units placed at the nodes of the face-centered cubic lattice. In the hypothesis that the behavior of these polymers is mainly determined by the high rigidity of the main chains, rather than by anisotropic attractive interactions, and that the side chains can be treated as completely flexible, the model requires a single adjustable parameter, related to the inflexibility of the main chain. Using the same value of this parameter for all the members of each series, the existence of stable anisotropic phases is predicted for the investigated systems, in good semiquantitative agreement with experiments. Furthermore, the values assumed in the two cases by the inflexibility parameter are of the same order as those which can be deduced from the average molecular dimensions for the two classes of polymers. We have also performed calculations modeling solutions of the two base polymers (without side groups) in which the volume fraction of the solvent equals the volume fraction occupied by the side groups in the bulk substituted polymers of the two series. The results indicate that the lowering of the isotropization temperature caused by the presence of flexible side chains is nearly coincident with that calculated for the corresponding solutions (without the demixing in two phases characteristic of solutions of rigid rods).

Introduction

Liquid-crystalline polymers have been the subject of extensive studies over the past two decades owing to their peculiar properties. In particular, quenching in the solid state the uniaxic structures characteristic of the mesophase allows preparation of fibers or films with anisotropic optical, mechanical, electrical, and magnetic properties.[1] This makes these polymers highly interesting from the technological and applicative standpoints.

A structural feature common to all the liquid-crystalline polymers is the relatively high degree of conformational stiffness. In particular, polymers characterized by very elongated and rigid chains are typically mesogenic. This is well known in the case of some para-aromatic polyamides, for instance, poly(1,4-benzamide) and poly(1,4-phenyleneterephthalamide),[2] which give mesophases in solutions and are utilized as high-modulus fibers. Similar characteristics (elongated shape and conformational stiffness) are found in para-aromatic polyesters like poly(1,4-oxybenzoyl) (PB) and poly(1,4-phenylene terephthalate) (PPT). These two polymers are then good candidates as examples of mesogenic polyesters. However, they are highly crystalline in the solid state, giving thermal degradation at the high temperatures necessary to obtain the liquids. Also, at variance with the corresponding polyamides, they are practically insoluble in common solvents.[3] Chemical modifications can be used to decrease the melting temperature and to stabilize the mesophase.[3,4] Two methods very useful to this end (allowing at the same time preservation of the linearity of the polymeric chain, which generally guarantees the obtainment of fibers having high Young's moduli) are the random introduction of rigid groups of different chemical nature along the main chain and the introduction of bulky side groups.[4] In the latter case, the resulting polymers give nematic mesophases on melting[5,6] and correspond to the general formulas


$\left[-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_3}(\mathrm{R})-\mathrm{O}-\right]_x$


$\left[-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_3}(\mathrm{R'})-\mathrm{C}(=\mathrm{O})\mathrm{O}-\mathrm{C_6H_3}(\mathrm{R''})-\mathrm{O}-\right]_x$

Polymers of the two series are indicated in the following with the symbols PB(R) and PPT(R′/R″), respectively, with R′ the substituent to the terephthalic ring and R″ the substituent to the hydroquinonic ring. Obviously, R = H and R′ = R″ = H in the case of the unsubstituted polymers.

The experimental results on polymers of the two series can be summarized as follows:

(1) As remarked in the review work of Dobb and McIntyre,[3] the substitution on the hydroquinonic rings of PPT derivatives is more effective than the substitution on the terephthalic rings in order to lower the melting temperature and to process the polymer in the nematic melt before decomposition (see also ref 7).

(2) According to the same authors,[3] the size (not the intrinsic chemical nature) of the lateral substituents plays the most important role in establishing the mesophasic behavior of polymers belonging to the two series. For instance, polyesters of the kind PPT(H/R″) with R″ = Cl or R″ = CH_3 give stable mesophases nearly in the same range of temperatures. On the other hand, polyesters of the same series with R″ = F are not mesogenic, while polyesters with bulkier side groups (OCH_3 or Br, for instance) show very narrow fields of stability of the mesophase.

(3) The melting and the isotropization temperatures of polyesters PPT(H/n-$(CH_2)_{n-1}CH_3$)[6] and PB(n-$(CH_2)_{n-1}CH_3$)[5] decrease steeply with increasing n for $n \leq 5$, while the decrease becomes much less pronounced for $n > 5$. A similar trend is shown by the series of low molecular weight nematogenic compounds synthesized and characterized by Weissflog and Demus in ref 8.

(4) The melting temperature of polyesters PPT-(H/n-$(CH_2)_{n-1}CH_3$ increases with increasing the degree of

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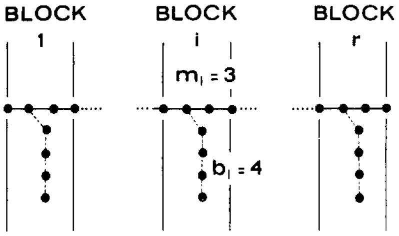


Figure 1. Schematic view of the lattice representation of a polymer chain. The full circles represent the centers of the isodiametric units; the continuous and broken lines connecting consecutive centers evidence the main chain and side chain segments, respectively. The vertical lines define a block. m_i is the number of units in the portion of the main chain belonging to the ith block; b_i is the number of units in the side chain belonging to the ith block.

polymerization, becoming almost constant for molecular weights higher than a critical value.[6]

The aim of the present paper is to understand the correlations between chemical structure and mesophasic properties of the title polymers within the frame of a very simple statistical-thermodynamical lattice model recently developed by us[7,8] to study the mesophasic behavior of liquid-crystalline polymers with rigid groups in the main chain or in the side chains and of semiflexible polymers with side chains having various lengths and degrees of inflexibility. In spite of the intrinsically approximate nature of the lattice representation, the comparison of predicted properties with experimental results can be made nearly quantitative, or at least semiquantitative, introducing the appropriate number of adjustable parameters related to various details of the chemical constitution of the polymers under study. However, in order to keep the model as simple as possible, we confine our attention in this work to a formulation with only one adjustable parameter, related to the inflexibility of the main chains. That is, a uniform degree of inflexibility is introduced along the main chains, the anisotropic attractive interactions are considered negligible with respect to the steric (excluded volume) effects, which are likely to predominate for polymers with highly stiff backbones, and the side chains are treated as completely flexible. We show in this paper that such a simplified model is able to predict the occurrence of isotropic/nematic phase transitions and the experimental trend of the transition temperatures for the two series of polymers PB(R) and PPT(R′/R″).

The Model

The polymer chains are represented in our model by sequences of isodiametric units placed at the nodes of a lattice. As shown in the next section, the polymer chains examined in the present paper can be roughly modeled as successions of blocks (see Figure 1), each block comprising a rodlike portion of the main chain and the side chain eventually attached to it. The composition of a general r-mer (see Figure 1) can be thus specified by the symbol $m_1(b_1)$–$m_2(b_2)$–...–$m_i(b_i)$–...–$m_r(b_r)$, with m_i the number of isodiametric units in the main chain portion of the ith block and b_i the number of the units in the corresponding side chain ($b_i = 0$ when the side chain is absent). The main chain is allowed to bend between consecutive blocks, with an energy penalty for noncollinear situations (see later). The present treatment is a particular application of the method developed by us for branched polymers in ref 9. The general features of the method can be summarized as follows:

(1) n_2 chains of x_t units (including those of the side chains) are allocated on a lattice comprising n_0 total sites. At variance with our previous treatments, n_0 can be greater than the product n_2x_t. The remaining $n_0 - n_2x_t = n_1$ sites can be empty or occupied by solvent molecules having the same dimensions of the chain units. Consecutive units of a lattice chain are placed on adjacent sites. Assuming a face-centered cubic lattice, each site has 12 first neighbors ($c = 12$, c being the lattice coordination number) and the segments connecting centers of consecutive units can assume six different orientations coinciding with the lattice directions $(x,x,0)$, $(x,0,x)$, $(0,x,x)$, $(x,\bar{x},0)$, $(\bar{x},0,x)$, and $(0,\bar{x},x)$. As a consequence, consecutive rods in the main chain, as well as consecutive segments in the side chains, may be placed on the lattice at an angle equal to 60°, 90°, 120°, or 180°. One of the lattice directions is considered special (direction z, coincident with the director in the nematic phase), the remaining directions being assumed equivalent to each other.

(2) The total partition function Z_t is written as the product of two terms, $Z_t = Z_{oc}Z_{st}$. Z_{oc} accounts for all the possible orientational states of the segments in the main chain and in the side groups, while Z_{st} accounts for repulsive (excluded volume) interactions. As we have shown in refs 10 and 11, attractive orientation-dependent interactions can be easily incorporated in our model, obviously leading to a better quantitative agreement of theoretical predictions and experimental results. However, this also implies the addition of one or more adjustable parameters in the calculations. We prefer then to neglect these interactions in the frame of the present approximate treatment, also based on the fact that both theory[12] and experiments[13] indicate that, in the case of rodlike oligomers having the same chemical nature of the backbone of PB and PPT, steric constraints are of greater consequence on the onset of the mesophase than the orientation-dependent interactions.

(3) The term Z_{oc} is evaluated under suitable orientational constraints using a product of matrices $\mathbf{U}'_i$ formally identical to the matrices $\mathbf{U}'_l$ of eq 1 in ref 9, with the difference that in the present case they are associated directly with the main chain rods belonging to the various blocks, rather than with each segment of the main chain. The product is extended over all the blocks (i is the running index of the blocks). That is

$$Z_{oc} = [\mathbf{J}^*(\prod_{i=1}^{r-1}\mathbf{U}'_i)\mathbf{J}]^{n_2} \qquad (1)$$

where $\mathbf{J}^*$ = row |1 0| and $\mathbf{J}$ = col |1 1|. The matrices $\mathbf{U}'_i$ contain the statistical weights of the orientational states of the ith rod with respect to those of the $(i-1)$th rod. Since one of the lattice directions is considered special, all the other $(c-2)/2 = 5$ directions being equivalent to each other, the order of the matrices is reduced to two. The first row and column correspond to orientations along the special z axis, while the second row and column correspond to orientations along the remaining equivalent five directions. In particular, when all the rods are made up of the same number of segments (all m_i's equal to m), they assume the form[9]

$$\mathbf{U}'_1 = \begin{vmatrix} \sigma^{\alpha_1-1}B_1 & 5\sigma^{\alpha_1}C_1 \\ \sigma^{\alpha_1-1}B_1 & 5\sigma^{\alpha_1}C_1 \end{vmatrix} \qquad (2)$$

and

$$\mathbf{U}'_i = \begin{vmatrix} \sigma^{\alpha_i-1}B_i & 10\epsilon_i\sigma^{\alpha_i}C_i \\ 2\epsilon_i\sigma^{\alpha_i-1}B_i & \sigma^{\alpha_i}(1+8\epsilon_i)C_i \end{vmatrix}, \quad i \neq 1 \qquad (3)$$

For instance, the element 1,1 of the matrix $\mathbf{U}'_i$ represents the statistical weight for the situation in which both the

$(i-1)$th and the ith segments are directed along z. The element 1,2 corresponds to the $(i-1)$th segment along z and the ith segment along one of the other $(c-2)/2 = 5$ directions, in such a way that the ith segment can be placed in $c-2 = 10$ different ways, each of these situations being associated with a bend. In the case of the element 2,1, the $(i-1)$th segment is directed along one of the five equivalent directions, while the ith segment can be placed in two different ways along the z axis. The element 2,2 represents the statistical weight for situations in which both segments are oriented along directions different from z. For a given direction of the $(i-1)$th segment, the two segments are collinear in one case, while a bend is realized in the remaining eight cases. In eqs 2 and 3 $\epsilon_i = \exp(-T^\circ_i/T)$, with kT°_i the energy needed to bend the chain between the $(i-1)$th and the ith rod (see later) and k the Boltzmann constant. α_i is the fraction of ith rods along the preferred z axis and σ a Lagrange multiplier allowing evaluation of Z_{oc} for various values of α, the fraction of segments along the preferred direction averaged over all the main chain and side chain segments. B_i and C_i represent the orientational partition functions of the segments belonging to the side group attached to the ith rod when the ith rod is placed along the preferred direction or along one of the remaining directions, respectively. They are evaluated using a product of matrices $\mathbf{U}'_{ik}$ (the same as the matrices $\mathbf{U}'_{lk}$ in ref 9, eq 4), containing the statistical weights of the orientational states of the kth segment of the side chain attached to the ith main chain rod with respect to those of the $(k-1)$th side chain segment:

$$\begin{vmatrix} B_i \\ C_i \end{vmatrix} = \left(\prod_{k=1}^{b_i} \mathbf{U}'_{ik}\right)\mathbf{J} \qquad (4)$$

where

$$\mathbf{U}'_{ik} = \begin{vmatrix} \sigma'^{\alpha_{ik}-1} & 10\epsilon_{ik}\sigma'^{\alpha_{ik}} \\ 2\epsilon_{ik}\sigma'^{\alpha_{ik}-1} & \sigma'^{\alpha_{ik}}(1+8\epsilon_{ik}) \end{vmatrix}, \quad k \neq 1 \qquad (5)$$

with an obvious meaning of the symbols $\epsilon_{ik} = \exp(-T^\circ_{ik}/T)$, T°_{ik}, and α_{ik}. α_{ik}, in particular, represents the fraction of kth segments oriented along z and belonging to the side chain attached to the ith rod. The factors σ' have the same meaning of the multipliers σ used in the matrices $\mathbf{U}'_i$ (eqs 2 and 3), allowing evaluation of Z_{oc} under orientational constraints.[9] In particular, when the fraction of segments along the preferred direction is required to be on average a prefixed value, α, the multipliers σ' are equal to $\sigma^{1/m}$.

The case $k = 1$ in the matrices $\mathbf{U}'_{ik}$ is special, since the spatial orientation of the first segment of a side chain is correlated to the spatial orientation of the rodlike portion of the main chain belonging to the same block. When the main chain rod is placed along z or is perpendicular to z, the first segment of the side chain cannot be directed along the z axis. For any other orientation of the main chain rod, the first segment of the side chain can be allocated along z or along three of the remaining directions. In total 20 different situations are accessible to this couple of segments when the ith rod is not directed along the z axis. Of these, only four take the first segment of the side chain along z. Hence

$$\mathbf{U}'_{i1} = \begin{vmatrix} 0 & 4\sigma'^{\alpha_{i1}} \\ (4/5)\sigma'^{\alpha_{i1}-1} & (16/5)\sigma'^{\alpha_{i1}} \end{vmatrix} \qquad (6)$$

(4) A partial inflexibility is introduced in the model using an energy penalty equal to kT°_i for consecutive noncollinear main chain rods (kT°_{ik} for side chain segments). Of course, T°_i (T°_{ik}) is 0 K in the completely flexible case, while $1/T^\circ_i$ ($1/T^\circ_{ik}$) is 0 K^{-1} in the completely inflexible case. In order to minimize the number of parameters, the side chains are assumed to be either completely flexible or totally inflexible in our calculations, while a single bending parameter, independent from the value of the angle and from the index i, is utilized for the main chains.

(5) The Z_{st} term can be identified with the number of ways to pack a mixture of chains of given average shape and orientation in the given volume, in such a way that the excluded volume condition is fulfilled. We use the counting scheme of Di Marzio,[14] in which the fraction of lattice sites available for the placement of a new segment in a given direction is assumed to coincide with the number of empty sites divided by the sum of empty sites plus the number of sequences (comprising one or more units) already placed in that direction. For linear chains, this leads to the formula (per mole of lattice sites):[15]

$$\begin{aligned} \ln (Z_{st}/RT) = {} & -(v_2/x)\ln(v_2/x) - (1-v_2)\ln(1-v_2) + \\ & [1 - v_2\alpha(x-1)/x]\ln[1 - v_2\alpha(x-1)/x] + \\ & [(c-2)/2]\{1 - v_2(1-\alpha)[2/(c-2)][(x-1)/x]\} \times \\ & \ln\{1 - v_2(1-\alpha)[2/(c-2)][(x-1)/x]\} \end{aligned} \qquad (7)$$

where x is the number of units in the chain, α is the fraction of segments along the preferred direction, and c is the lattice coordination number. As in ref 9, we make the approximation that eq 7 can also be used for branched chains such as those modeled in this paper, provided that x is substituted by x_t, the total number of units in the chains (including the side groups), and α is averaged over all the main chain and the side chain segments.

(6) The model allows evaluation of the total partition function (and the Helmholtz free energy, $A = -RT \ln Z_t$) for various orientational distributions of the segments. In practice, for a given value of σ introduced within the matrices $\mathbf{U}'_i$ and $\mathbf{U}'_{ik}$, the fraction of main and side chain segments along the preferred direction can be evaluated according to the methods explained in ref 9. That is, for a given σ, each α_i is given by $Z_{oc}{}^*(i)^{1/n_2}$ (the sum of statistical weights of all the states having the ith rod along z) divided by $Z_{oc}{}^{1/n_2}$ (the sum of the statistical weights of all the possible states of the chain); each α_{ik} is given by $Z_{oc}{}^*(i,k)^{1/n_2}$ (the sum of the statistical weights of all the states having along z the kth segment belonging to the side chain attached to the ith rod) divided by $Z_{oc}{}^{1/n_2}$. $Z_{oc}{}^*(i)^{1/n_2}$ (or $Z_{oc}{}^*(i,k)^{1/n_2}$) is obtained with the same product of matrices giving Z_{oc}, but replacing with zero the elements of the second column in $\mathbf{U}'_i$ (or in $\mathbf{U}'_{ik}$). This allows evaluation of Z_{oc}, the orientational distribution of all the chain segments, Z_{st}, and hence Z_t for each given σ.

Of course, the thermodynamically stable phase corresponds to the orientational distribution of segments which makes the free energy a minimum. There is always a minimum, corresponding to the isotropic or to the anisotropic phase. When two minima are found, they correspond to the isotropic and to the anisotropic phases. In these cases, the anisotropic phase may be thermodynamically stable (absolute minimum) or metastable (relative minimum).

Lattice Modeling of Polymer Chains

The polymers studied in this paper are poly(1,4-oxybenzoyl) (PB) or poly(1,4-phenylene terephthalate) (PPT) chains with phenyl or n-alkyl side groups. They can be modeled as lattice chains of the kind shown in Figure 1 on the basis of simple geometrical and energetic considerations. Figures 2 and 3 show polyesters PB and PPT,

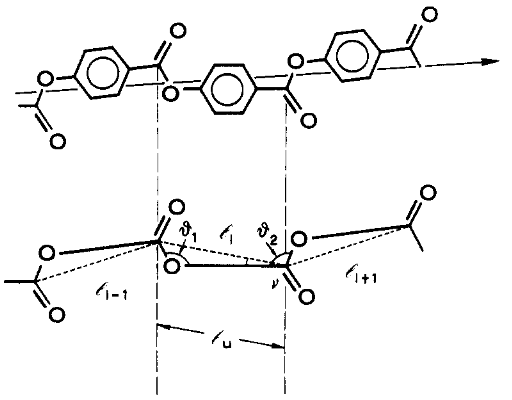


Figure 2. Schematic view of the chain of poly(1,4-oxybenzoyl) (PB) in extended conformation.

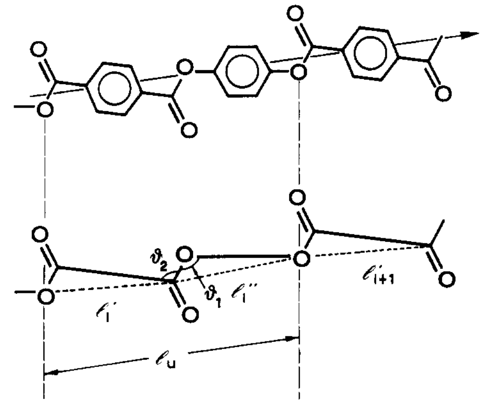


Figure 3. Schematic view of the chain of poly(1,4-phenylene terephthalate) (PPT) in extended conformation.

Table I
Some Geometrical Constants of PPT and PB[a]

PB	PPT
$l = 0.644$ nm	$l' = l'' = 0.637$ nm
$\theta_1 = 110.9°$	$\theta_1 = 110.9°$
$\theta_2 = 118.3°$	$\theta_2 = 118.3°$
$l_u (=l) = 0.644$ nm	$l_u = 1.24$ nm
20 (ref 23) $< C_\infty <$ 238 (ref 16) (300 K)	20 (ref 23) $< C_\infty <$ 238 (ref 16) (300 K)

[a] Reference 16. The symbols are defined in Figures 1 and 2.

respectively, drawn in extended conformations. According to Flory and co-workers,[16] the two bonds connecting each phenylene ring to the polymer chain are collinear with the axis of the ring. Also, the ester bonds can be considered rigid and transplanar. A PB chain (see Figure 2) can be then schematically described as a sequence of virtual bonds of length l connecting the carbon atoms of consecutive ester groups. A PPT chain (see Figure 3) can be described as an alternating sequence of virtual bonds of lengths l' (connecting the –O– oxygen of an ester group to the carbon of the subsequent ester group and encompassing a terephthalic ring) and l'' (connecting the carbon of an ester group to the –O– oxygen of the subsequent ester group and encompassing a hydroquinonic ring). In all cases, the virtual bonds lie in the plane defined by the axis of the phenylene rings and the CO–O ester bond. Some relevant characteristics of PB and PPT are reported in Table I, showing that l, l', and l'' are approximately equal (0.64 nm).

The previous considerations allow us to consider the lattice chains modeling the polyesters of the two series as made of blocks, each block comprising the (rigid) portion of the main chain spanned by a virtual bond and the side chain eventually attached to it. The number of lattice units in a given portion of the chain (main chain or side groups) can be evaluated as the ratio of the volume occupied by that portion of chain and the volume available to each unit on the face-centered cubic lattice. The latter is given by $d^3/\sqrt{2}$, with d the distance of two neighboring lattice sites. To establish a suitable value for the parameter d, we consider a segment of polymer chain surrounded by six locally parallel neighbors. The area per chain in a plane perpendicular to the direction of the segments is $d^2/\sqrt{2}$ (four of the six neighbors are at a distance $\sqrt{3}d/2$ and the two at a distance d). Hence, the density of the system is $\delta = (\sqrt{2}M_u/l_uN_Ad^2)$, where M_u is the mass of the repetition unit, l_u is the average length of the projection of this unit along the local chain axis, and N_A is Avogadro's number.[15,17] In the case of liquid PB and PPT, with δ between 10% and 15% less than the room temperature crystalline density of PB (1480 kg/m^3 [18]) and with l_u as given in Table I, the value of d is of the order of 0.58–0.60 nm. A similar value (0.6 nm) has been extrapolated in ref 19 from a plot of the average diameter of PPT chains with two n-alkyl side groups for each terephthalic ring vs the length of the latter. The same value (0.59 nm) is obtained for amorphous polyethylene using δ = 850 kg/m^3 and l_u = 1.1 Å.[20] On these bases, we assume that the portion of main chain belonging to a block of the lattice chains modeling both PB and PPT comprises 1.1 lattice units. The number of units for an n-alkyl side chain of n carbon atoms is given by $0.027n/0.145$, 0.027 nm^3 being the average volume per CH_2 group in the amorphous state and 0.145 nm^3 being the volume per lattice site in the model system. Also, on the basis of crystallographic data,[21] we assume equal to 1 the number of units corresponding to a phenyl side group.

A note is made here of the fact that a noninteger number of units in the rigid groups or in the flexible parts is obviously incompatible with a lattice representation. We make the reasonable hypothesis that the properties of systems with parts comprising a noninteger number of units are intermediate between those evaluated for the analogous systems with the closest integer lengths of the various groups. This is easily done in the case of the rigid groups, whose length appears in our formulas as a simple multiplicative factor. The same is not true for the flexible parts, since the number of units constituting a flexible group appears in our equations as the upper index of a matrix product. The properties of systems of this kind are then obtained by interpolation (see also ref 15).

The repetition unit of the lattice chains modeling the polyesters of the series PB(R) coincides with a single block. Hence, the corresponding polymer chain will be indicated as $[1.1(b)]_r$, where 1.1 represents the number of isodiametric units constituting the main chain portion of each block, b is the number of isodiametric units constituting the side chain associated to the block, and r is the degree of polymerization. In the case of the polyesters PPT-(R′/R″), the repetition unit of the corresponding lattice chains comprises two consecutive blocks. Hence, the symbol $[1.1(b')\text{–}1.1(b'')]_{r/2}$ will be used to indicate the corresponding lattice polymer, b' and b'' being the number of isodiametric units in the side groups R′ and R″, respectively.

An order of magnitude for the parameter T°, associated with a bending between consecutive blocks of the lattice chains modeling the polyesters PB and PPT, may be selected in such a way that the mean square end-to-end distance of the lattice chains in the isotropic phase be coincident with that of the corresponding polymers in unperturbed conditions. According to ref 22 (p 25), the mean square end-to-end distance of a long chain constituted by n identical bonds with separable configurational energies (that is, the total configurational energy is a sum of separate contributions depending on the bond angle (Θ_i) and on the torsional angles (Φ_i) at each individual bond, i) is given by

$$\langle r^2\rangle_0 = nl^2[(\mathbf{E} + \langle\mathbf{T}\rangle)(\mathbf{E} - \langle\mathbf{T}\rangle)^{-1}]_{11} \qquad (8)$$

where l is the bond length, $\mathbf{E}$ is the identity matrix of third order, and $\langle\mathbf{T}\rangle$ is the statistical mechanical average of the matrix:

$$\mathbf{T}_i = \begin{vmatrix} -\cos\Theta_i & \sin\Theta_i & 0 \\ -\sin\Theta_i\cos\Phi_i & -\cos\Theta_i\cos\Phi_i & \sin\Phi_i \\ \sin\Theta_i\sin\Phi_i & \cos\Theta_i\sin\Phi_i & \cos\Phi_i \end{vmatrix}$$

The signs have been changed to account for the fact that Θ_i is the bond angle here (instead of its supplement in ref 22) and for the non-IUPAC notation used in ref 22 for the torsional angles. The subscript 11 in eq 8 indicates the first element of the first row in the resulting matrix. Equation 8 is obviously applicable to the lattice chains considered in this work. In fact, these chains are a succession of blocks having all the same length. The angle at the junction of two blocks can assume several values in our model (60°, 90°, 120°, and 180°), the value at a given junction being uncorrelated to that at any other junction (in the isotropic phase). The latter is also true for the dihedral angles defined by three consecutive blocks, with the further simplification that the values of Θ_i and Φ_i are completely uncorrelated in the case of the lattice chains. This implies that terms of $\mathbf{T}_i$ containing Θ_i and terms containing Φ_i can be separately averaged to give the matrix $\langle\mathbf{T}\rangle$ of eq 1. Also, owing to the lattice symmetry and to the fact that all the allowed dihedral angles are equiprobable in our model, $\langle\sin\Phi_i\rangle = \langle\cos\Phi_i\rangle = 0$, in such a way that eq 8 reduces to

$$\langle r^2\rangle_0 = nl^2(1 - \langle\cos\Theta_i\rangle)/(1 + \langle\cos\Theta_i\rangle) \qquad (9)$$

Since an energy penalty is included in our model for a bending between consecutive blocks, the value of $\langle\cos\Theta_i\rangle$ depends on the temperature. There are 11 ways of realizing a junction in the face-centered cubic lattice, 10 of which (4 at 60°, 4 at 120°, and 2 at 90°) are associated with a bending. Since $\cos(60°) = -\cos(120°)$ and $\cos(90°) = 0$, $\langle\cos\Theta_i\rangle = -1/(1 + 10\epsilon)$, with $\epsilon = \exp(-T^\circ/T)$. As a result, the mean square end-to-end distance of the lattice chains considered in this work in the isotropic phase is simply given by $nl^2(1 + 5\epsilon)/5\epsilon$.

The characteristic ratios of PB and PPT are likely to be in the range 20–230 at 300 K, where the upper bound corresponds to the value deduced in ref 16 with the ester bond rigid and transplanar and with fixed valence angles, while the lower bound corresponds to the value calculated in ref 23 allowing torsional fluctuations around the ester bond and fluctuations of the valence angles Ph–CO–O and CO–O–Ph. Experimentally, the characteristic ratio determined by light scattering for poly(phenylhydroquinone-*co*-terephthalic acid) is in the range 20–50.[24] A reasonable value of T° for the lattice chains investigated in this paper is then in the range 1400–2000 K. It is useful to emphasize here that these large values of T° are related to the fact that the polymers are modeled as lattice chains, the allowed angles between consecutive blocks being dictated by the geometry of the lattice. Values as large as 60°, 90°, and 120° are obviously unrealistic for PB and PPT, in which the angles between consecutive virtual bonds are quite small. In other words, the overall shape of a chain is modeled on the lattice with a smaller number of larger angles, which requires high values of T°.

Table II
Experimental Melting (T_m) and Isotropization Temperature (T_{ni}) of Some Derivatives of PPT[a] and Results Obtained for the Corresponding Lattice Chains

	exptl			calcd[b]	
PPT(R′/R″)	T_m, K	T_{ni}, K	lattice chain	$(T/T^\circ)_{ni}$	$10^{-3}T^\circ$, K
PPT(H/H)	>900[c]		$[1.1\text{–}1.1]_{r/2}$	0.54	>1.7
PPT(Ph/Ph)[d]	*e*	504	$[1.1(1)\text{–}1.1(1)]_{r/2}$	0.28	1.8
PPT(H/Ph)	619	748	$[1.1\text{–}1.1(1)]_{r/2}$	0.34	2.2
PPT(Ph/H)	560	642	$[1.1\text{–}1.1(1)]_{r/2}$	0.34	1.9

[a] Reference 7. [b] Calculations are made for $r = 100$. [c] Determined through DSC measurement with heating rate >80 K/min, in order to minimize the effect due to the thermal degradation. [d] Ph represents a phenyl group. [e] Noncrystalline polymer, showing a glass transition at 395 K.

Results and Discussion

The principal aim of this work is to investigate the ability of the lattice model to capture the essential aspects of the mesophasic behavior of the title polymers. Within the frame of our approximate treatment, this behavior depends on the lengths of the rigid portions of the main chain and of the side chains, as well as on the inflexibility parameter of the main chain, T° (the side chains are considered either completely flexible or completely inflexible). T° is the only adjustable parameter of our model. In particular, for a given constitution of the lattice chains, the Helmholtz free energy is a function of the ratio T/T°. For each of the polymers modeled in this paper, we have deduced the value of T/T° for which the isotropic and the anisotropic phases are in equilibrium, and then the values of T° for which the experimental and calculated isotropic/nematic transition temperatures coincide. The lattice model can be considered a good approximation if, within a given series of polymers, a single value of T° is able to explain the experimental trend of the transition temperatures. Also, this value of T° should be in the range 1400–2000 K (see before).

The calculations reported in this paper have been performed at constant volume. The change of volume associated with nematic/isotropic phase transitions is very small, and at least in a first approximation can be neglected. In practice, unless specified otherwise, all the lattice sites are assumed occupied, the fraction of occupied sites v_2 ($=n_2x_t/n_0$) being placed equal to 1 when using eq 7. That is, the free volume is incorporated in the volume of the lattice sites, which is also implicit in the calculation of the lattice constant d shown in the previous section. A more detailed treatment of the free volume, which requires substantial modifications of the model, would be out of proportion in the frame of this simple, approximate theory. The ordered phases found stable in our calculations are characterized by alignment of the main chains along the nematic director (coincident with the z axis of the lattice), while the orientation of the side chains is nearly isotropic.

First of all, we have applied the model to polyesters of the series PPT(R′/R″) with R′ and/or R″ the phenyl group or H. Table II shows the experimentally observed melting and isotropization temperatures of some of these polymers,[7] the symbols identifying the lattice constitution of the corresponding lattice r-mers ($r = 100$), the calculated isotropization temperatures (divided by T°), and the values of T° giving the best agreement with the experiments. The latter are close to 2000 K, that is of the order of the higher bound of the range 1400–2000 K. In particular, using $T^\circ = 2000$ K, the nematic/isotropic transition tem-

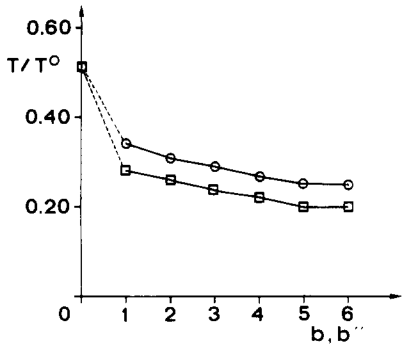


Figure 4. Calculated isotropic/nematic transition temperatures (divided by T°) of r-mers $[1.1(b)]_r$ (squares) and $[1.1\text{–}1.1(b'')]_{r/2}$ (circles), with $r = 100$, vs b and b'', respectively ($v_2 = 1$, lattice coordination number = 12, side chains completely flexible).

perature predicted for the system of lattice chains modeling unsubstituted PPT is equal to 1100 K, well above the decomposition temperature of this polymer. The different value assumed by T° for the last two polymers in Table II reflects the fact that this simple and approximate model is unable to distinguish the different location of the hydrogen and of the phenyl group in the two cases. In fact, the two polymers are represented by the same lattice chain.

Figure 4 plots the calculated values of the ratio T/T° vs b and b'', the number of isodiametric units comprised in the side groups of the lattice chains $[1.1(b)]_r$ (squares) and $[1.1\text{–}1.1(b'')]_{r/2}$ (circles). All the calculations have been performed for r-mers with $r = 100$ and with completely flexible side chains. For both series of polymers, the isotropization temperature decreases steeply for the addition of a short substituent (b or $b'' = 1$), while a further increase of the length of the side groups causes a much smaller decrease of T/T°. This behavior is in good agreement with the experimental trend of the transition temperatures observed for polyesters of the two series in refs 5 and 6 and for the classes of low molecular weight nematogens having similar constitutions studied in ref 8. When $b = b''$, the isotropization temperature of the lattice chains $[1.1(b)]_r$ is always lower than the isotropization temperature of the lattice chains $[1.1\text{–}1.1(b'')]_{r/2}$. This is obviously associated with the smaller proportion of side chains in the second case (one branch every other block) than in the first case (one branch per block).

We take into consideration now the series of polyesters $PB(n\text{-}(CH_2)_{n-1}CH_3)$ with n = 5, 6, 10, 12, 14, 16, and 18[5] and $PPT(H/n\text{-}(CH_2)_{n-1}CH_3)$ with n = 6, 7, 8, and 10.[6] The systems in the first series show smectic-like mesophases for $n \geq 6$.[25] A similar behavior has been found for other polymers with a rigid backbone and flexible side chains when the length of the latter is greater than a critical value (for a review, see ref 19), the formation of these smectic-like phases being due to the tendency of the alkyl groups to segregate from the rigid backbones. Many of these polymers also show in the solid state phase transitions in which the side groups become conformationally disordered. Since the smectic-like nature of the mesophases does not imply substantial order of the side groups (considered to act as a "bound solvent" by Ballauff in ref 19), our theory can be applied to these systems without modifications.

The systems of refs 5 and 6 are characterized by non-integer values of b and b'', respectively. In the reasonable hypothesis that the properties of these systems are intermediate between those of the analogous systems with the closest integer side chain length, the plots in Figure 4 can be interpolated to give the values of T° which would reproduce the experimental isotropization temperatures. These are listed in Tables III, together with the experimental isotropization temperatures of the corresponding polymers. T° is close to the higher limit established before (2000 K) in the case of the lattice chains modeling the derivatives of PB, slightly lower in the case of the lattice chains modeling the derivatives of PPT.

Table III
Experimental Isotropization Temperatures (T_{ni}) of Some Polyesters $PB(n\text{-}(CH_2)_{n-1}CH_3)$[a] and $PPT(H/n\text{-}(CH_2)_{n-1}CH_3)$[b] and Values of T° Giving the Experimental T_{ni} (As Deduced from Figure 4) for the Lattice Chain (r = 100) Modeling Each Polymer

n	T_{ni}, K	lattice chain	$10^{-3}T^\circ$, K
		$PB(n\text{-}(CH_2)_{n-1}CH_3)$	
5	618	$[1.1(0.93)]_r$	2.0
6	545	$[1.1(1.1)]_r$	2.0
10	503	$[1.1(1.9)]_r$	1.9
12	498	$[1.1(2.2)]_r$	1.9
14	485	$[1.1(2.6)]_r$	2.0
16	475	$[1.1(3.0)]_r$	2.0
18	475	$[1.1(3.4)]_r$	2.1
		$PPT(H/n\text{-}(CH_2)_{n-1}CH_3)$	
6	596	$[1.1\text{–}1.1(1.1)]_{r/2}$	1.7
7	575	$[1.1\text{–}1.1(1.3)]_{r/2}$	1.7
8	581	$[1.1\text{–}1.1(1.5)]_{r/2}$	1.8
10	592	$[1.1\text{–}1.1(1.9)]_{r/2}$	1.9

[a] Reference 5. [b] Reference 6.

Table IV
Calculated Isotropization Temperatures (Divided by T°) of the Indicated Lattice r-Mers (r = 100) in Two Extreme Cases, i.e., with Side Chains Completely Flexible and Completely Inflexible

	$(T/T^\circ)_{ni}$	
b,b''	flexible side chains	inflexible side chains
	$[1.1(b)]_r$	
0	0.54	0.54
1	0.28	0.28
2	0.26	0.21
3	0.24	0.16
4	0.22	*a*
5	0.20	*a*
6	0.20	*a*
	$[1.1\text{–}1.1(b'')]_{r/2}$	
0	0.54	0.54
1	0.34	0.34
2	0.31	0.28
3	0.29	0.25
4	0.27	0.23
5	0.25	*b*
6	0.25	*b*

[a] The ordered phase is characterized by the inflexible side groups aligned with z, the main chain segments lying along the remaining directions even in the limit $1/T = 0\ K^{-1}$. [b] Same as in (a), with the difference that the distribution of main chain segments becomes nearly isotropic at very high temperatures.

Table IV compares the results obtained for the systems $[1.1\text{–}1.1(b'')]_{r/2}$ and $[1.1(b)]_r$ (r = 100) when the side groups are assumed completely flexible with those calculated treating the side groups as rigid rods. In the case of lattice chains of the kind $[1.1(b)]_r$, the isotropization temperatures calculated assuming rigid side groups are predicted to be slightly smaller than those calculated with flexible side chains when $b = 2$ or $b = 3$. The nematic phase is characterized in these cases by main chain segments preferentially aligned along the nematic director and by an isotropic distribution of the (rigid) side group segments. When $b \geq 4$, a different kind of molecular arrangement is found in the nematic phase, with the side groups preferentially aligned along the nematic director and the

Table V
Comparison of Isotropic/Nematic Transition Temperatures

A. Comparison of $(T/T^\circ)_{ni}$ Calculated for Lattice r-Mers $[1.1\text{–}1.1(b'')]_{r/2}$ and $[1.1(b)]_r$ When $v_2 = 1$ with $(T/T^\circ)_{ni}$ of r-Mers $[1.1]_r$ ($r = 100$) When $(1 - v_2)^a$ Coincides with the Volume Fraction Occupied by the Side Chains in the First Cases

$[1.1\text{–}1.1(b'')]_{r/2}$		$[1.1]_r$		$[1.1(b)]_r$		$[1.1]_r$	
b''	$(T/T^\circ)_{ni}$	$(1 - v_2)$	$(T/T^\circ)_{ni}$	b	$(T/T^\circ)_{ni}$	$(1 - v_2)$	$(T/T^\circ)_{ni}$
0	0.54	0	0.54	0	0.54	0	0.54
1	0.34	0.31	0.36	1	0.28	0.48	0.31
2	0.31	0.48	0.31	2	0.26	0.65	0.26
3	0.29	0.58	0.28	3	0.24	0.73	0.24
4	0.27	0.65	0.26	4	0.22	0.78	0.22
5	0.25	0.69	0.25	5	0.20	0.82	0.21
6	0.25	0.73	0.24	6	0.20	0.85	0.21

B. Comparison of $(T/T^\circ)_{ni}$ Calculated for Lattice r-Mers $[1.1\text{–}1.1(b'')]_{r/2}$ and $[1.1(b)]_r$ When $v_2 = 1$ with $(T/T^\circ)_{ni}$ of r-Mers $[1.1\text{–}1.1(1)]_{r/2}$ and $[1.1(1)]_r$ ($r = 100$), Respectively, When $(1 - v_2)^a$ Coincides with the Volume Fraction Occupied in the Formers by the Side Chain Units Other Than the First

$[1.1\text{–}1.1(b'')]_{r/2}$		$[1.1\text{–}1.1(1)]_{r/2}$		$[1.1(b)]_r$		$[1.1(1)]_r$	
b''	$(T/T^\circ)_{ni}$	$(1 - v_2)$	$(T/T^\circ)_{ni}$	b	$(T/T^\circ)_{ni}$	$(1 - v_2)$	$(T/T^\circ)_{ni}$
0	0.54			0	0.54		
1	0.34	0	0.34	1	0.28	0	0.28
2	0.31	0.24	0.29	2	0.26	0.32	0.24
3	0.29	0.38	0.27	3	0.24	0.49	0.22
4	0.27	0.48	0.25	4	0.22	0.59	0.20
5	0.25	0.56	0.24	5	0.20	0.66	0.19
6	0.25	0.61	0.23	6	0.20	0.70	0.18

[a] $(1 - v_2)$ = volume fraction of solvent.

main chain segments distributed along the other lattice directions. No isotropization point is found for $b \geq 4$. In other words, lattice chains belonging to this series with rigid side groups longer than 3 isodiametric units are ordered even in the limit $1/T = 0\ \mathrm{K}^{-1}$, that is when the angles between the main chain blocks are unrestricted. A similar behavior is shown by lattice chains of the series $[1.1\text{–}1.1(b'')]_{r/2}$, with the difference that the critical length of the rigid side groups for the onset of the latter kind of mesophase is $b'' = 5$. As before, this is related to the smaller density of side groups in these systems.

It is well-known that, in the case of polymers with rigid and flexible groups alternating along the main chain, the flexible parts play an active role in the onset of the mesophase.[26] On the contrary, there are several experimental indications that the effect on the mesophasic behavior of adding flexible side groups to the title polymers is similar to that of adding a corresponding amount of a solvent, without the demixing in isotropic and anisotropic phases characteristic of lyotropic solutions. This is also predicted by our lattice model, as shown in Table V. Table VA compares the ratios T/T° at the isotropic/nematic transition of r-mers $[1.1\text{–}1.1(b'')]_{r/2}$ and $[1.1(b)]_r$ ($r = 100$, $v_2 = 1$) with those of the r-mer $[1.1]_r$ ($r = 100$), calculated when $(1 - v_2)$, the fraction of lattice sites occupied by a solvent, coincides with the volume fraction occupied by the side chains in the bulk systems. Analogous calculations are reported in Table VB, where the results obtained for the two series of bulk r-mers are compared with those for the corresponding lattice solutions of r-mers with short side groups ($b = b'' = 1$). The isotropization temperatures of the bulk systems and of the corresponding lattice solutions are quite similar in all the cases examined, indicating that the side chains do indeed act as a diluent in the sense explained above.

Finally, we have examined the effect of different degrees of polymerization on the nematic/isotropic transition temperature of the lattice systems. The results are shown in Figure 5, where the isotropization temperatures (divided by T°) of r-mers $[1.1\text{–}1.1(b'')]_r$ with $b'' = 2$ and $b'' = 3$ are plotted as a function of the degree of polymerization r (logarithmic scale). The side chains have been assumed completely flexible, and v_2 has been set equal to 1. Figure 5 shows that (1) the isotropization temperature increases with r for $r \leq 10$, (2) the isotropization temperature becomes nearly constant in the range $10 \leq r < 100$, and (3) the isotropization temperature of r-mers with $b'' = 2$ is always higher than the isotropization temperature of r-mers with $b'' = 3$.

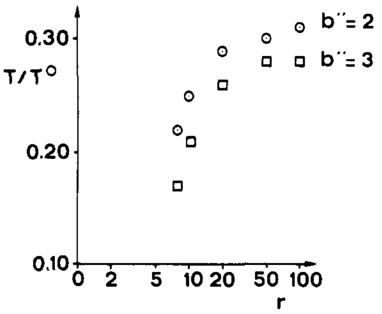
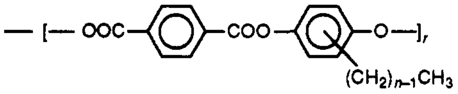


Figure 5. Calculated isotropic/nematic transition temperatures (divided by T°) of r-mers $[1.1\text{–}1.1(b'')]_{r/2}$ vs r (logarithmic scale, $v_2 = 1$, lattice coordination number = 12, side chains completely flexible).

These trends are in very good agreement with the experimental behavior evidenced in ref 6 for oligomers of the kind


$$-[-\mathrm{OOC}-\mathrm{C_6H_4}-\mathrm{COO}-\mathrm{C_6H_3}((\mathrm{CH_2})_{n-1}\mathrm{CH_3})-\mathrm{O}-]_r$$

with n = 6, 7, 8, and 10.[6]

Conclusions

We have implemented in this work a simple lattice model of the mesophasic behavior of polymers constituted by sequences of rigid, rodlike groups, eventually substituted with flexible or rigid side chains. For a given constitution of the main chain, the model requires a single adjustable parameter, T°, which represents a measure of the degree of inflexibility of the main chain (the higher T°, the higher the inflexibility). We have applied the model to two series of polyesters, derived from PB and PPT. The value of T° for which the mean square end-to-end distance of the lattice chains modeling PB and PPT coincides with that of the unperturbed polymers is contained in both cases in the range 1400–2000 K. We have shown that the lattice model allows calculation of isotropization temperatures in good agreement with experiments in all the cases examined, using values of T° within this range. In particular, the best value of T° is close to the higher limit (2000 K) in the case of derivatives of PB, while it is slightly lower in the case of derivatives of PPT. This could be taken as an indication that the backbones of polyesters PPT(R′/R″) and PB(R) are characterized by almost the same degree of inflexibility.

Our calculations indicate that the nematic/isotropic transition temperature of the studied systems does not depend substantially on the degree of inflexibility of the side chains (for side chains shorter than a critical length). On the other hand, the isotropization temperatures evaluated in the presence or in the absence of side chains, the side groups being substituted by a solvent in the latter case, are not very different. This confirms that the mesogenic, low-temperature tractable polymers which are required in most practical applications can be obtained from high-melting rodlike polymers by suitable chemical substitution, other than by dissolving them in a solvent. The chemical substitution method can be more advantageous in all the cases in which the demixing in two phases characteristic of solutions of rigid rods has to be avoided. Of course, this method is especially appropriate for highly insoluble polymers like PB and PPT. In this respect, our results indicate that low isotropization temperatures can be obtained more efficiently by substituting the backbone with many short side groups than with fewer, but longer side chains.

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Registry No. PPT (R′ = H, R″ = H) (copolymer), 26618-60-0; PPT (R′ = Ph, R″ = Ph) (copolymer), 133216-33-8; PPT (R′ = H, R″ = Ph) (copolymer), 67203-03-6; PPT (R′ = Ph, R″ = H) (copolymer), 139242-72-1; PPT (R′ = H, R″ = H) (SRU), 26637-45-6; PPT (R′ = Ph, R″ = Ph) (SRU), 95935-20-9; PPT (R′ = H, R″ = Ph) (SRU), 67256-36-4; PPT (R′ = Ph, R″ = H) (SRU), 80302-60-9; PB (n = 5) (homopolymer), 120411-51-0; PB (n = 6) (homopolymer), 119865-15-5; PB (n = 10) (homopolymer), 119865-17-7; PB (n = 12) (homopolymer), 119865-19-9; PB (n = 14) (homopolymer), 119865-21-3; PB (n = 16) (homopolymer), 119865-23-5; PB (n = 18) (homopolymer), 119865-25-7; PB (n = 5) (SRU), 120411-52-1; PB (n = 6) (SRU), 119865-56-4; PB (n = 10) (SRU), 119865-57-5; PB (n = 12) (SRU), 119865-58-6; PB (n = 14) (SRU), 119865-59-7; PB (n = 16) (SRU), 119865-60-0; PB (n = 18) (SRU), 119865-61-1; PPT (R′ = H, R″ = $(CH_2)_5CH_3$) (copolymer), 115258-44-1; PPT (R′ = H, R″ = $(CH_2)_6CH_3$) (copolymer), 139242-73-2; PPT (R′ = H, R″ = $(CH_2)_7CH_3$) (copolymer), 131930-51-3; PPT (R′ = H, R″ = $(CH_2)_9CH_3$) (copolymer), 115258-45-2; PPT (R′ = H, R″ = $(CH_2)_5CH_3$) (SRU), 89190-73-8; PPT (R′ = H, R″ = $(CH_2)_6CH_3$) (SRU), 89190-74-9; PPT (R′ = H, R″ = $(CH_2)_7CH_3$) (SRU), 89190-75-0; PPT (R′ = H, R″ = $(CH_2)_9CH_3$) (SRU), 89190-77-2.