Communications to the Editor

Evidence of Topological Interaction among Polymers: A_2 of Ring Polymers in the Θ-State

Recently, high molecular weight, narrow-distribution ring polystyrene (PS) has been synthesized by Roovers and Toporowski, and it has been found that this polymer has a fairly large osmotic second virial coefficient, A_2, in a Θ-solvent (cyclohexane at 35 °C).[1] Since the excluded volume effect disappears in a Θ-solvent, this A_2 must come from the topological repulsive force discussed in the previous papers (TDFRP-I[2] and -II[3]);[4] it may be called the "topological second virial coefficient".[2]

Topological states of ring polymers are described by Gauss' linking number, τ, which represents the degree of entwining between two loops (Figure 1).[2,3] Intermolecular interaction among polymers is repulsive as an average when $\tau = 0$ and attractive when $\tau \neq 0$ (Figure 1).[2] This "topological force" comes from the restriction that τ should be kept constant for any deformation of the polymers. Since polymer networks are composed of numerous loops and since the τ's for all possible pairs of the loops in the networks should also be kept constant, large topological forces are acting inside networks; this is a new way of describing entanglement in rubber-elasticity,[5] a concept about which there is at present active discussion.[6] We have presented a theory of rubber-elasticity based on the topology of loops and shown that the topological force can be regarded as the main source of rubber-elasticity.[5] It is the most direct demonstration of the existence of the topological force that A_2 for ring polymers does not disappear in the Θ-state. The experiment of Roovers and Toporowski[1] is just what is expected. From their experiment, we can determine a parameter, $\bar{\gamma}$, the "topological interaction parameter for repeat units", which represents the entanglement ability of PS.

Second Virial Coefficient in the Θ-State. Let a and b be ring polymers which are in a topological state τ and let $P_\tau(\mathbf{w})$ be the distribution function of $\mathbf{w}$, the relative coordinate vector between their centers of mass. The topological force acting between them is defined by $f_\tau = -kT(\partial \ln P_\tau(\mathbf{w})/\partial \mathbf{w})$, which is repulsive for $\tau = 0$ and attractive for $\tau \neq 0$. In the Roovers–Toporowski experiment,[1] the ring polymers are all in the state $\tau = 0$ so that the repulsive force is acting among them. Although excluded volume forces also act among polymers, they disappear in the Θ-state and A_2 must then come purely from the topological repulsive force. The second virial coefficient in the Θ-state, A_2^Θ, is then given by

$$A_2^\Theta = (N_A/2M^2) \int [1 - P_0(\mathbf{w})] \, d\mathbf{w} \tag{1}$$

where N_A is Avogadro's number and M is the molecular weight of the polymer. In TDFRP-I and -II, $P_\tau(\mathbf{w})$ has been expressed in terms of contact probabilities of submolecules. Numerical calculation of A_2^Θ has also been done in TDFRP-I, but it is not accurate enough for the present quantitative study, because the contact probabilities used were those for infinitely long chains. In this work, A_2^Θ is computed again using exact expressions of the contact probabilities for finite numbers n of submolecules per chain.

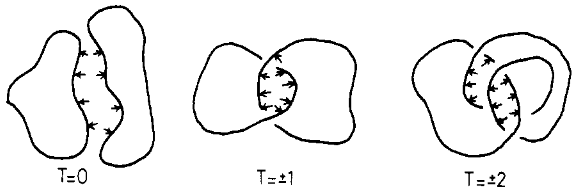

Figure 1. Topological states of two ring polymers. Average intermolecular interaction is repulsive when $\tau = 0$ and attractive when $\tau \neq 0$.

Topological Interaction Parameter for Repeat Units. In the topological theories of rubber-elasticity,[5] of viscoelasticity,[7] and of ring polymers,[2,3] a common parameter, γ, the "topological interaction parameter for submolecules", appears which represents the entanglement ability of the submolecules. The definition of γ is a little different according to whether the submolecules are introduced in the final stage (TDFRP-I) or in the beginning (TDFRP-II) of the formulation. The definition of TDFRP-I, which is the more strict, is adopted here; but a little modification is necessary for applying it to real chains. Let b_i^a and b_j^b be the ith and jth bond vector of the main chain of polymer a and b, respectively, and Θ_{ij} be τ for bond pair (b_i^a, b_j^b). The "correlation length along the polymer chain" is defined so that $\langle \Theta_{ij}\Theta_{i'j'} \rangle$ disappears for $|i - i'| > \epsilon$ or $|j - j'| > \epsilon$ (an explanation of ϵ has been given in TDFRP-I). In real polymer chains, repeat units (or "monomers") are usually composed of several bond vectors, say, $b_l^a, b_{l+1}^a, ..., b_{l+s-1}^a$ or $b_m^b, b_{m+1}^b, ..., b_{m+s-1}^b$, where s is length of the repeat units and l and m are their heads. The quantity $\gamma_{2;1,1}$ introduced in TDFRP-I (cf. eq 3.4a.I and 3.4b.I)[8] is generalized to real polymer chains as follows:

$$\bar{\gamma} = (V/\bar{b}^3) \sum_{i=l}^{l+s-1} \sum_{i'=l}^{l+s+\epsilon} \sum_{j=m}^{m+s-1} \sum_{j'=m}^{m+s+\epsilon} \langle \Theta_{ij}\Theta_{i'j'} \rangle \tag{2}$$

where $\bar{b}$ is the effective bond length per repeat unit, V is volume of the system, and the angular brackets represent an equilibrium average for infinitely long chains. The topological interaction parameter for submolecules, which are composed of ν repeat units, is given by[2]

$$\gamma = \nu^2\bar{\gamma} \tag{3}$$

The length of the submolecules, ν, may be chosen arbitrarily if the following conditions are satisfied:

$$\nu s > \epsilon, \quad n \gg 1 \tag{4}$$

Since ν is uncertain, so is γ, while $\bar{\gamma}$ is defined uniquely; $\bar{\gamma}$ may be therefore used as a molecular parameter representing entanglement ability of polymer chains and is called the "topological interaction parameter for repeat units". The parameter $\bar{\gamma}$ depends on the chemical structure of the chains; roughly speaking, the more flexible and thinner the polymer chains are, the larger it is. It has been found in TDFRP-I that $\bar{\gamma}$ for 6-choice simple cubic lattice model polymers (SCLMP) is equal to 0.0495. (In this polymer, $\bar{\gamma}$ is identical with $\gamma_{2;1,1}$). For real polymer chains, however, it is difficult, though not impossible, to compute $\bar{\gamma}$ theoretically, and at present $\bar{\gamma}$ is considered to be an empirical parameter determined, say, by measurement of A_2^Θ. It must be noted that in general $\bar{\gamma}$ depends also on the excluded volume effect; what is discussed here is $\bar{\gamma}$ in the Θ-state only, and an expression of $\bar{\gamma}$ for nonzero excluded volume is not known. It is, however, $\bar{\gamma}$ in the Θ-state that is required in rubber-elasticity and viscoelasticity, because the concentration of polymers considered there is usually so high that the excluded volume effect can be neglected.

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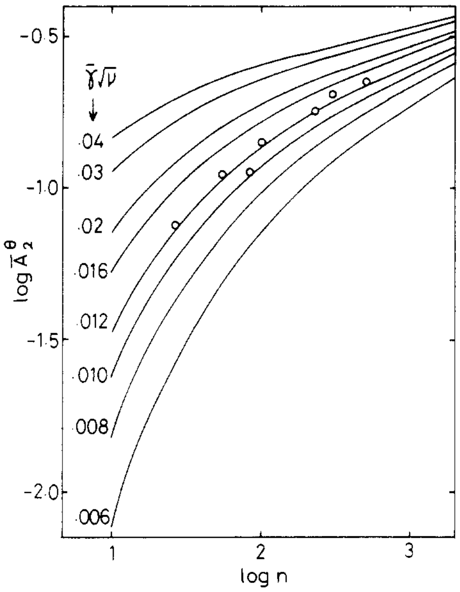

Figure 2. log–log plot of reduced topological second virial coefficient, $\bar{A}_2^\Theta$ vs. n. Numbers attached to curves represent $\bar{\gamma}\nu^{1/2}$. Open circles are experimental data of Roovers and Toporowski for polystyrene in cyclohexane at 35 °C;[1] they are fitted to the theoretical curve for $\bar{\gamma}\nu^{1/2} = 0.012$.

Results and Discussion. It is convenient to introduce a reduced second virial coefficient, $\bar{A}_2^\Theta = (2M^{1/2}M_0^{3/2}/N_A\bar{b}^3)A_2^\Theta$, which is a function of n and $\bar{\gamma}\nu^{1/2}$ alone; here M_0 is the molecular weight of the repeat units. Calculation of A_2^Θ is done in almost the same way as in TDFRP-I: A_2^Θ is defined by eq 1, and $P_0(\mathrm{w})$, G^{I}, and G^{II} are given by eq 4.19b.I, 4.9.I, 4.10a,I, and 4.10b.I; the only difference is in the calculation of the contact probabilities for submolecules, $P(0_{00}|\mathrm{w})$ and $P(0_{ij}|0_{00},\mathrm{w})$ which is done by using exact expressions for finite n instead of using the approximate eq 4.7a.I and 4.7b.I (which are exact only for $n \to \infty$). Results of calculation[9] are shown in Figure 2, in which log $\bar{A}_2^\Theta$ is plotted against log n for various $\bar{\gamma}\nu^{1/2}$. In plotting experimental data in Figure 2, the ordinate (log $\bar{A}_2^\Theta$) is determined uniquely but the abscissa (log n) is uncertain by an amount log ν. The Roovers–Toporowski data for PS agree well with theoretical curves for $0.008 \le \bar{\gamma}\nu^{1/2} \le 0.020$ ($\bar{b} = 0.72_0$ nm is assumed). This leads to $3.72 \le \nu \le 23.4$ and $\bar{\gamma} = 0.0041_4$. As an example, data for $\nu = 8.51$ are shown in Figure 2 by open circles, which are in good agreement with a theoretical curve for $\bar{\gamma}\nu^{1/2} = 0.012$. It is important here that (1) the same $\bar{\gamma}$ (=0.0041) is obtained for $3.72 \le \nu \le 23.4$ (2) conditions (4) are roughtly satisfied by this ν. It is interesting to compare this result with that of the 6-choice SCLMP,[2] of which bond vectors are in effect connected by free joints and which may therefore be considered as a standard model polymer: comparison of $\bar{\gamma}$ of these polymers shows that one free jointed bond (of the 6-choice SCLMP) corresponds to 3.4_6 $(=(0.0495/0.0041_4)^{1/2})$ repeat units of PS, a results which seems reasonable considering that bond angles are fixed and bulky side groups are attached to the main chain of PS. In rubber-elasticity, typical polymers are not PS but polyisoprene, polybutadiene, or poly(dimethylsiloxane), but their $\bar{\gamma}$ are not known at present because there are no data for their A_2^Θ. Ring poly(dimethylsiloxane) has been already synthesized and A_2 has been measured in good solvents but, unfortunately, A_2^Θ has not.[10] It is expected that A_2^Θ of many other polymers will be measured in the future.

Registry No. PS (homopolymer), 9003-53-6.

References and Notes

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(8) Equations of TDFRP-I are indicated by attaching the symbol .I to the equation numbers.
(9) A detailed numerical table of $\bar{A}_2^\Theta$ is available from the author on request.
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Phase Separation in Polyurethanes—A Deuterium NMR Study

Although numerous models have been set forth concerning the morphological microdomain structure for polyurethanes,[1] there is at present no consensus in this matter. Bonart et al.,[2-5] on the basis of wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) experiments, have proposed hard segment packing models in which the hard segments assume fully extended configurations within lamellar or sheetlike domains. This model is represented schematically in Figure 1a. Subsequent WAXS studies by Blackwell et al.[6] supported this model.

However, recent results by Van Bogart et al.[7] and Koberstein and Stein[8] are inconsistent with an extended sequence model. Using SAXS, both groups of investigators find that the hard segment chains must be present in either coiled or perhaps folded configurations. Koberstein and Stein developed a new model based on these results.[8] In this model, the hard segment domain thickness is governed predominantly by the shortest hard segment sequence length that is insoluble in the soft segment phase. Sequences longer than this critical length adopt coiled configurations to reenter the hard segment domain and fill space efficiently. Further detailed SAXS experiments on a series of polyurethanes of varying hard segment content support this model.[1] The Koberstein–Stein model is represented schematically in Figure 1b.

In this communication we present data that further define the nature of phase separation and hard-segment phase mixing in polyurethanes. In particular, our results address the following questions: (1) What fraction of the hard segment has motional characteristics identical to the pure hard segment material? (2) How does this fraction change as a function of the weight percent of hard component? and (3) How do the deuterium NMR data compare with the results of SAXS?

We have shown previously that solid-state deuterium NMR spectroscopy[9-12] is an exceptionally powerful tool for addressing the molecular details of phase separation in segmented copolyesters.[13,14] Deuterium NMR discriminates on the basis of molecular motion between those hard segments that are identical with the pure hard segment

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