Communications to the Editor

Anomaly in the Molecular Weight Dependence of Surface Tension of Molten Polyethers and Polyesters. Evidence of Chain Folding?

Currently the most popular concepts concerning the structure of undiluted amorphous polymers are incorporated into the "bundle" model of Kargin,[1] Flory-Bueche's model of "entangled" statistical coils,[2,3] and the chain-folding model of Robertson.[4] A detailed description of the above models can be found in the original papers.[1-4] The point of interest here is that each model requires radically different packing of macromolecules in the bulk and we propose the differences described below. Supposing that the "true-polymer"-like properties of macromolecules begin to manifest themselves after arrival at a characteristic molecular weight interval, M_p, the dependence of molecular packing density, *PD*, on M in terms of Kargin's model can be represented by the schematic drawing in Figure 1a. Next, taking into consideration that each "entanglement" point in the form of an intermolecular "knot" in the Flory-Bueche model stands for a local packing defect, the number of "entanglements" in the unit volume being essentially constant[2,5] the dependence of *PD* on M for this model can be represented by Figure 1b. Finally, in Robertson's model each flexed portion of the chain in the fold also tends to lower *PD*, but in this case one may expect a regular increase in the size of ordered regions in the chain-folded entity as M increases.[6,7] Dependence of *PD* on M for this model is shown in Figure 1c. It is clear that the validity of these models could be tested in principle by direct measurements of densities, ρ, of polymer fractions with different M's; but unfortunately, the accuracy of existing experimental methods seems to be too low to detect such delicate effects. In our opinion, measurements of surface tension are preferable for this purpose, since by virtue of the empirical Sugden's rule, $\gamma = (P\rho/M)$,[4] where γ is the surface tension and P is the parachor,[8] the sensitivity of γ to small changes in *PD* should be much higher than that of the macroscopic density, ρ (however, see below).

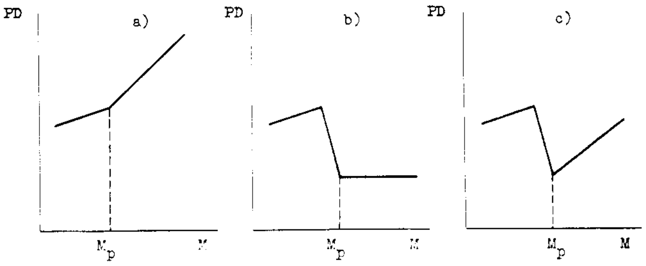

Figure 1. Schematic representation of the molecular packing density-molecular weight relationship according to Kargin's model (a), Flory-Bueche's model (b), and Robertson's model (c).

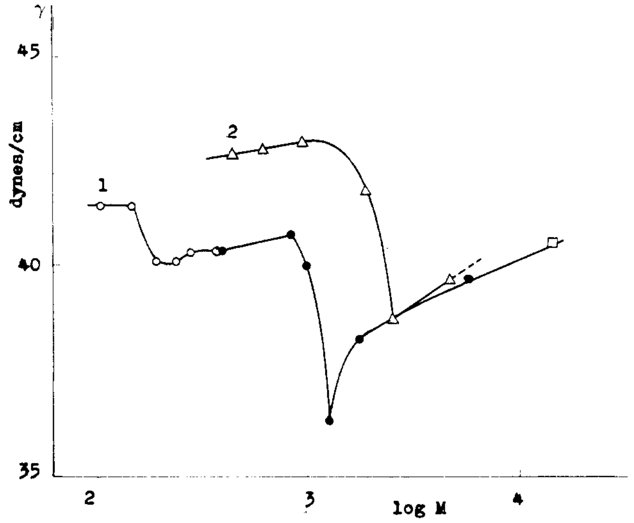

Figure 2. Dependence of surface tension on log M for PEO at 80° (curve 1) and PDA at 25° (curve 2): open circles, individual glycols; closed circles, triangles, and square, fractions.

With the aid of a modified Wilhelmy method,[9] we studied the surface tension at 80° of mono-, di-, tri-, tetra-, penta-, hexa-, and octaethylene glycols, as well as narrow fractions of poly(ethylene oxide) (PEO) with viscosity-average molecular weights, M_v, of 400, 840, 1070, 1300, 1530, 6300, and 14,800 (for the last sample the value of γ was estimated from the concentration dependence of γ in water solutions according to the procedure outlined in ref 10). The Wilhelmy method appears to be especially appropriate for our purpose due both to its high accuracy (in this work estimated to be better than 0.3%) and to its inherent ability of additional cleaning of the liquid-air interface. No special precautions were taken to avoid the possibility of polymer melt oxidation during its exposure to air at 80° for about 20-30 min (the time interval of a single experiment) since it seemed very unlikely that this effect, even if real, would differentially affect different samples. Moreover, indirect evidence (constancy of surface tension and melt viscosity of fractions in the repeated runs at 80°, as well as identical values of molecular weights prior to and after former experiments) suggests that in this case oxidation or other related chemical changes were virtually absent.

The results obtained are plotted in Figure 2, where we also show similar data for poly(diethylene glycol adipates) (PDA) from an earlier paper.[11] It is immediately seen that the experimental curves for both polymer series exhibit pronounced minima at M_v = 1300 (PEO) and at M = 2500 (PDA). The observed dependence is drastically different from the postulated[12] smooth increase of γ with M. On the other hand, it rather nicely conforms to the dependence of *PD* on M as required by the chain-folding model (Figure 1c). Evidently, a sudden drop of experimental γ values at $M_v > 830$ for PEO, and at $M > 10^3$ for PDA, reflects a sharp loosening of molecular packing which accompanies the "nucleation" of fluctuating folds in the system. Different positions of minima in the γ-M curves, corresponding to the stabilization of the most probable folded conformation, are to be attributed to the intrinsic differences in molecular structure of PEO and PDA. A final gradual rise of γ with a further increase of M according to the foregoing analysis can be explained by a higher molecular packing density in the melt as a result of a regular increase of dimensions of ordered regions in folded-back macromolecules.[6,7] Our present data, therefore, are in gratifying qualitative agreement with recent results of Godovskii *et al.*[13] according to which the onset of chain folding during crystallization of PEO fractions from the melt, also corresponds to the range of M from 1500 to 2000.

We note, in conclusion, that the experimental values of

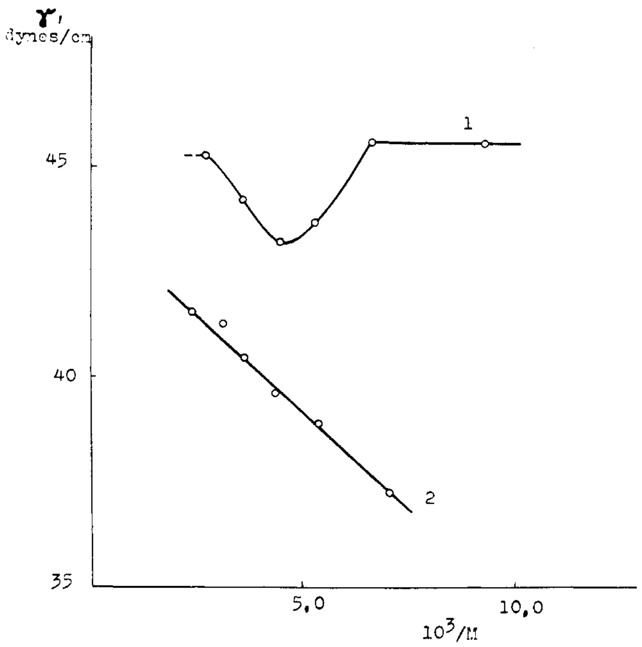

Figure 3. Dependence of surface tension at 25° on M^{-1} for OH-terminated glycols (curve 1) and for Cl-substituted samples (curve 2).

at 80° for monomeric glycols also pass through the broad minimum at the pentamer (see Figure 2). In order to elucidate the origin of this anomaly we have also measured surface tension at 25° both for these glycols as well as for the corresponding liquids in which terminal hydroxyls were substituted with chlorine. It can be seen from Figure 3 that for OH-terminated samples the minimum of γ^{25} has become more pronounced as compared with the corresponding data for 80°, while the values of γ^{25} for Cl-substituted liquids exhibit the typical linear dependence on M^{-1} for an end-group effect.[2] Thus, it can be safely concluded that the minimum value of γ in OH-terminated glycols is brought about by the competing effects of lowering of the hydrogen-bond concentration and of a simultaneous increase in the chain length. Therefore, absence of such anomaly for Cl-substituted samples suggests that sharp minima of γ^{80} in the high molecular weight region (*i.e.*, at 1300 for PEO and at 2500 for PDA) are not affected by end groups and should be attributed to an intramolecular transition, presumably from an extended into a folded-chain conformation.

It is worth noting that according to the Parachor relation the observed minima in surface tension values would require corresponding density changes in respective samples, whereas our data at 25° for lower (individual) homologs of PEO[14] as well as data of Ingham *et al.*[15] for PEO fractions at 75° show that in the respective series the density is a constant within the claimed experimental uncertainty (1.121 ± 0.002 g/cm^3 for the former and 1.080 ± 0.002 g/cm^3 for the latter). However, this discrepancy must not be regarded as being crucial as it first seems to be since a Parachor is not a quantitatively exact relation and many deviations are reported in the literature. Therefore, we conclude that this relation may be applied with reasonable accuracy only for those liquids which have similar structural (packing) features (in the case considered here well below and/or above the observed anomalies). If this condition is not satisfied, then the quantitative Parachor equation ceases to apply, although even in such a case a certain correlation between γ and ρ may still be expected to exist. However, its establishment must wait for further thorough work.

Summary

The results of experimental studies of surface tension in a series of narrow PEO fractions demonstrate the sensitivity of this parameter to structural changes in undiluted amorphous polymers, which are believed to reflect the transition from extended into folded conformation of macromolecules on the arrival at some characteristic molecular weight interval. Moreover, striking similarity of γ-M dependence for a crystallizing polymer, PEO, and for a noncrystallizable one, PDA, suggests that chain-folding phenomenon is a universal property of both crystallizing and noncrystallizing polymers in the amorphous state.

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References and Notes

(1) V. A. Kargin and G. L. Slonimskii, "Brief Outlines on the Physical Chemistry of Polymers," Khimia, 1967 (in Russian), Moscow.
(2) F. Bueche, "Physical Properties of Polymers," Interscience, New York, N. Y., 1962.
(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
(4) R. E. Robertson, *J. Phys. Chem.*, **69**, 1575 (1965).
(5) G. C. Berry and T. G. Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).
(6) V. P. Privalko, 8th Prague IUPAC Microsymposium, Aug 1971, Abstract C2.
(7) V. P. Privalko, Yu. V. Pasechnik, L. I. Bezruk, and Yu. S. Lipatov, *Vysokomol. Soedin., Ser. B*, **15**, 381 (1973).
(8) F. B. Garner and S. Sugden, *J. Chem. Soc.*, 1298 (1929).
(9) A. E. Feinerman, Yu. S. Lipatov, and V. M. Kulik, *Kolloid. Zh.*, **32**, 620 (1970).
(10) Yu. S. Lipatov and A. E. Feinerman, *J. Adhesion*, **3**, 3 (1971).
(11) A. E. Feinerman, Yu. S. Lipatov, and V. K. Maistruk, *Dokl. Akad. Nauk SSSR*, **178**, 1129 (1968).
(12) G. L. Gaines, Jr., *Polym. Eng. Sci.*, **12**, 1 (1972).
(13) Yu. K. Godovskii, N. M. Garbar, and G. L. Slonimskii, *Vysokomol. Soedin., Ser. A*, **15**, 813 (1973).
(14) A. P. Lobodina, I. A. Popov, and V. P. Privalko in "Sintez i Fiziko-Khimia Polimerov," Naukova Dumka, Kiev, 1973, Issue No. 15.
(15) J. D. Ingham and D. D. Lawson, *J. Polym. Sci., Part A*, **3**, 2707 (1965).

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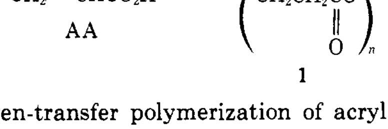
Hydrogen-Transfer Polymerization of Acrylic Acid to Poly(β-propiolactone)

This paper describes a new finding of the hydrogen-transfer polymerization of acrylic acid (AA) to polyester (**1**) of β-hydroxypropionic acid.



$$\underset{\text{AA}}{CH_2{=}CHCO_2H} \longrightarrow \left(CH_2CH_2\overset{}{\underset{\underset{O}{\|}}{C}}O\right)_n \qquad (1)$$

1

The hydrogen-transfer polymerization of acrylamide with base catalyst has been reported for the first time by Breslow *et al.*[1] Thus, poly(β-alanine) was synthesized from acrylamide (eq 2).

$$CH_2{=}CHCONH_2 \longrightarrow \left(CH_2CH_2CONH\right)_n \qquad (2)$$

Very recently we have reported alternating copolymerization of 2-oxazoline with AA to give a copolymer of the