at the upper end of the MWD. As limited by the accuracy of our viscosity measurements, it is worthwhile to note that there is no "linear" polymer in BPE-I, while BPE-II and BPE-III contain about 15% "linear" polymer each at the low end of the MWD. The same trends may be followed in branching values calculated using the other equations.

We can now speculate on the cause of departure from ideal polymerization behavior, particularly in BPE-I and BPE-III. A growing chain with the normal terminal $R(CH_2)_xCH_2\cdot$ can disappear by addition with monomer, by termination, or by either of the two chain-transfer mechanisms leading to branching. Other transfer reactions occur but are not of interest here. The *intramolecular* transfer would probably be assisted by increasing the temperature and by increasing the conversion if the latter proceeded to the point of significant monomer depletion. Again, the *intermolecular* transfer to polymer is assisted by increased temperature and assuredly by higher conversion.

It would be helpful if we could associate molecular weight with degree of conversion or residence time, but the assumptions necessary are obviously unrealistic. The following brief comments are therefore strictly qualitative and oversimplified.

In stirred autoclaves, polymerization conditions in terms of *T*, *P*, and [M] are likely to be the most constant. The greatest variable would be the residence time of a given polymer molecule. Thus, for BPE-II, the increase in LCB at very high molecular weight would represent molecules with the longest residence time, and the apparently "linear" low molecular weight end would represent the shortest residence times. The SCB levels would be unaffected by residence time.

Tubular reactors, on the other hand, vary widely in *T* and *P*, with less variation in residence time, and unusual distributions might be expected. For BPE-I the reactor temperature was apparently uniform enough to maintain normal levels of SCB. This leaves pressure perhaps as the main variable, with monomer depletion a secondary factor. Applying the same line of reasoning, perhaps temperature is the major variable in the manufacture of BPE-III in light of the wide variation in SCB.

Based on experimental data, some authors have indicated that a single gel permeation chromatography calibration curve may be used to provide true molecular weight distributions for a variety of branched polyethylenes.[7,11] Two conditions must be met for this to be strictly true. The variations in λ_{LCB} within a sample must be negligible, and variations between different samples must not be greater than, say, a factor of 3. Our data indicate that the first condition will not be met by a wide population of representative commercial polyethylenes. Thus, while a branched-polymer calibration curve will give truer values of MWD than a linear-polymer calibration, precise MWD analysis requires prior knowledge of the type of branch distribution.

Conclusions

Application of the universal calibration concept to gel permeation chromatography data allows relatively reliable measurement of LCB in commercial polyethylenes. When combined with infrared analysis of the total methyl group content, reasonable values for SCB may also be derived. Acceptance of a molecular-weight-independent branching coefficient for all commercial branched polyethylenes seems an oversimplification, especially in the case of tubular reactor products. This limits the applicability of a single gel permeation chromatography calibration curve where precise MWD is sought.

Acknowledgments. The authors thank J. P. Luongo and Mrs. G. Pasteur for the infrared determination of total branching.

Notes

Desorption of Polystyrene from Silica Gel Thin Layer Chromatography Substrates

E. P. Otocka,*[1a] P. M. Muglia,[1a] and H. L. Frisch[1b]

Bell Telephone Laboratories, Incorporated,
Murray Hill, New Jersey 07974, and State University of New York,
Albany, New York 12203. Received February 24, 1971

It has recently been found that synthetic polymers can be effectively fractionated by thin layer chromatography (tlc).[2,3] This work further explores the mechanisms by which such fractionation occurs.

Both solubility and adsorption effects have been identified as playing a role in the tlc fractionation of polymers. For successive adsorption–desorption cycles to play a major part in separation of molecules according to their molecular weight, the rates of these processes must be quite rapid, since the experimental time is less than 1 hr. Normally determined desorption rates are orders of magnitude slower,[4] which suggests that desorption cannot play a significant role in the tlc fractionation of polymers.

The following method was employed to examine desorption rates of polystyrene from tlc substrates. Commercial precoated plastic-backed tlc plates of silica gel with zinc silicate fluorescent indicator (Brinkmann Instrument Co.) were cut into 3 × 8 cm sections. Aliquots (15 μl) of anionically polymerized polystyrenes (Pressure Chemical Co.) in CCl_4 (1 mg/ml) were applied as ~0.3 × 1.0 cm streaks to give a calculated average adsorbent coverage of 4×10^{-4} mg cm^{-2}.

The plates were not given any special drying treatment. While this results in a small amount of water adsorbed on the plate, our previous experience indicates that the removal of water by standard activating procedures does not markedly decrease R_f values observed during elution. The plates employed in earlier work were not activated.[2]

---

[1] (a) Bell Telephone Laboratories; (b) State University of New York.

[2] (a) E. P. Otocka and M. Y. Hellman, *Macromolecules*, **3**, 362 (1970); (b) E. P. Otocka, *ibid.*, **3**, 691 (1970).

[3] F. Kamiyama, H. Matsuda, and H. Ingaki, *Polym. J.*, **1**, 518 (1970).

[4] W. H. Grant and R. R. Stromberg, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 1397 (1970).

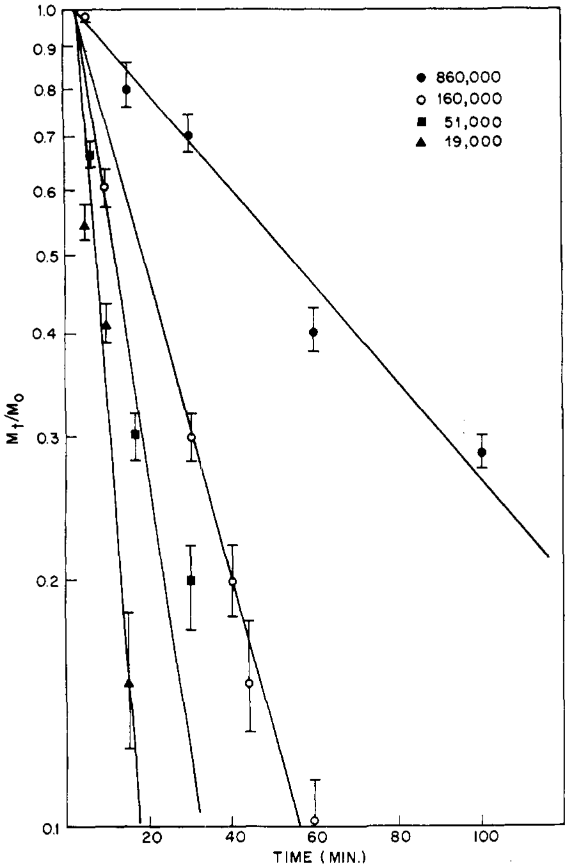

Figure 1. Desorption of polystyrenes from silica gel tlc substrate in benzene.

The spotting solvent, CCl_4, was settled upon because the applied material appeared as a roughly gaussian deposit: the concentration measured by the densitometer was greatest in the center of this bar, decreasing smoothly toward the edges. More polar (eluting) solvents gave a polymer deposit deficient in the center and more concentrated at the edges. These observations indicate to us that adsorbtion occurs during spotting.

After drying, the tlc strips were scanned with an SD 3000 densitometer (Schoeffel Instrument Co.) at 265 mμ with a 0.1 × 0.8 cm slit. The polymer appears as dark bars on the bright fluorescent background. It has been shown that the integrated area recorded by the densitometer under these conditions is proportional to the amount of polymer. The tlc strip was then completely immersed in solvent (benzene or CCl_4). After various immersion times the substrates were removed, dried, and rescanned. In additional experiments, the solvent in which the tlc strip was immersed was vigorously stirred by a magnetic stirring bar.

Figure 1 shows the results of desorption in static benzene. The data can be represented by

$$\log M_t/M_0 = -K_D(t - t_s) \qquad (1)$$

where M_t is the weight of polymer after immersion time, t; M_0 is the initial weight of polymer present; and t_s is about 2 min. The origin of t_s presents some question. We feel that it represents the time needed to resolvate and rearrange the dried polymer layer before desorption can proceed.

The values of K_D are plotted as a function of molecular weight in Figure 2 according to

$$-K_D = AM^a \qquad (2)$$

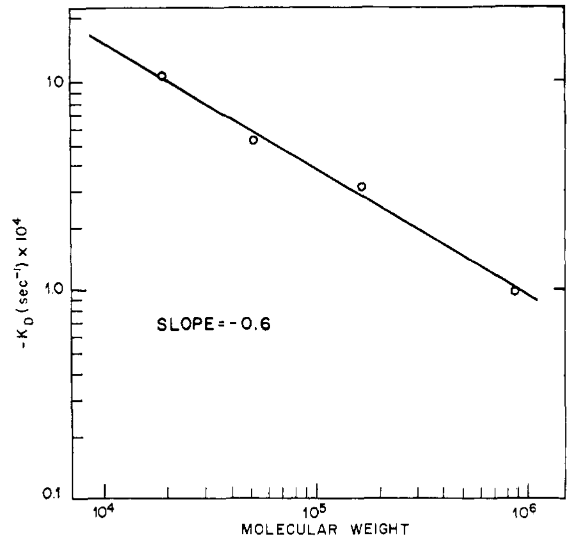

Figure 2. Desorption rate constants as a function of molecular weight (silica gel–benzene).

with a value of a of -0.60 found to fit the line.

This value of -0.6 does not give an unambiguous definition of the rate-determining step. The diffusion coefficients for polystyrene depend on the -0.53 power of the molecular weight,[5] and the molecular weight dependences of specific adsorption or adsorbed layer thicknesses also have fractional exponents.

The concentration profile across the original polymer deposit was roughly gaussian. This profile was retained after partial desorption but in a slightly broader form. The half-width at time t, W_t, minus the original half-width, W_0, is plotted as a function of time for several molecular weights in Figure 3. While the data do not permit conclusive analysis, it appears likely that the spot dimensions are broadened by simple diffusion. It is also possible, however, that desorption from the more concentrated central portion of the deposit is significantly faster than at the edges, which also will result in broadening the concentration profile.

The apparent desorption rates are sensitive to several factors. The nature of the desorbing solvent is quite important. Desorption rates in CCl_4 were much lower than in benzene. For example, the 1.98×10^4 sample desorbs

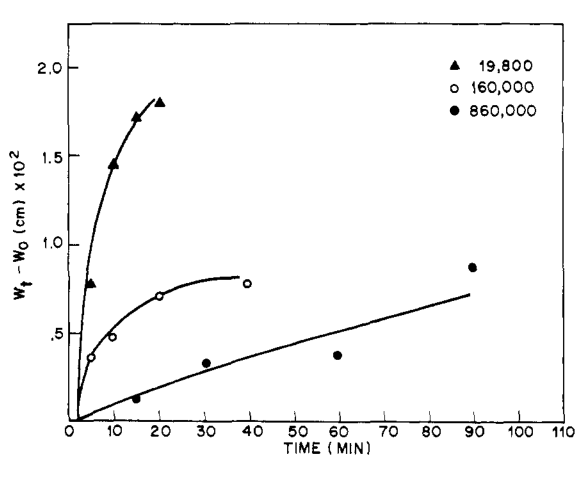

Figure 3. Half-widths of residual polymer layers as a function of time (silica gel–benzene).

---

[5] G. Meyerhoff, *Z. Phys. Chem. (Frankfurt Am Main)*, **4**, 335 (1955).

in CCl_4 at a slower rate than the 8.60×10^5 sample in benzene. It has been observed that CCl_4 is a noneluting solvent for polystyrene on silica gel.[2a] From this it is tempting to relate chromatographic mobility directly to desorption rate. This is an obvious oversimplification, because all the fractions studied here elute completely with benzene ($R_f = 1.0$) despite marked differences in their desorption rates in the static solvent.

Stirring tremendously enhances desorption rates. In stirred benzene the 1.60×10^5 sample is lost more rapidly than the 1.98×10^4 polymer in the same static solvent. In addition, it was possible to establish that the residue was displaced significantly (several millimeters in some cases) from its original position. The cause of enhanced desorption may arise from increased concentration gradients above the adsorbed layer as the flowing liquid removes desorbed molecules. Momentum transfer between the flowing solvent and partially desorbed molecules may also be significant. The appearance of material on substrates remote from the initial coverage is indicative of rapid readsorption of displaced polymer. While quite remote, it is not impossible that the adsorbed macromolecules have been displaced without desorption. One can picture an isolated molecule acting somewhat like a tumbleweed, moving even though a number of segments are always in contact with the substrate. In actual chromatographic experiments, it is doubtful whether momentum transfer could be significant because of low solvent velocities. However, the transport of desorbed species is a well-known feature in tlc for conventional molecules.

Several important conclusions may be drawn from these results. The desorption of polymer from tlc substrates is rapid enough and sensitive enough to molecular weight to play a major part in the fractionation observed in tlc of polymers. The reason for rapid desorption in these experiments remains a matter of conjecture. At the present time, our hypothesis is that the method of applying the material, *i.e.*, spotting and drying, results in a decreased number of solute–substrate attachments per molecule compared to conventional adsorption.

Acknowledgment. The authors wish to thank T. K. Kwei and R. J. Roe for several helpful discussions.

Communications to the Editor

A New Kind of Polymeric Material Obtained by the Rigidification of Heterophase Block Copolymer–Solvent Systems

In this communication we describe a new class of rigid polymeric materials which, although they appear homogeneous on visual inspection, reveal *periodic* microstructure when examined by the low-angle X-ray technique or by electron microscopy. It is hoped that many of these novel materials will have practical value, and work aimed at their utilization is being carried out in this laboratory.

The technique developed by Szwarc[1] for preparation of living polymers permits the synthesis of block polymers having structures such as A–B or A–B–A, in which A and B denote the sequences of monomers a and b, respectively. This method also allows one to vary the size of individual blocks.[2] Using this approach, we prepared many block polymers and thoroughly examined their behavior in solvents, S, which preferentially dissolve one of the component blocks. It has been demonstrated[3–7] that a system may acquire various structures, depending on temperature; on the size, composition, and nature of the block polymer; and on the choice of solvent, as indicated by the phase diagram shown in Figure 1.[8] At very low concentration, the block polymer dissolves in S and a conventional solution of A–B in S is then formed. Irregularly located aggregates of A–B appear in the solution when the concentration of the block polymer increases to a few per cent. The insoluble blocks, B, then form cores surrounded by soluble chains of A. At still higher concentrations (20–30%), the aggregates coalesce into regular and periodic structures. Three types of structures have been revealed by low-angle X-ray diffraction, namely lamellae, hexagonally packed cylinders, and, less frequently, cubically packed spheres. The "insoluble" blocks form the "solid" phase, while the soluble blocks are mixed with the solvent, as shown in Figure 2.

The structural parameters, obtained from X-ray analysis, depend on the nature and sizes of the blocks as well as on the nature and proportion of the solvent. For example, the thickness of the layers may vary from 200 to 800 Å, the diameters of cylinders may be 80–400 Å, and the distance between their axes may range from 200 to 700 Å. Although many systems were examined and some empirical rules were established, a comprehensive theory of these systems is not yet available in spite of several attempts[9,10] to develop one.

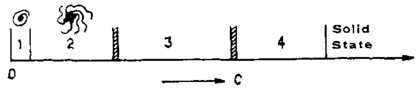

Figure 1. A schematic phase diagram as generally observed in (A–B)S systems, at growing concentrtaions of copolymer: (1) pure solution (monomolecular micelle); (2) aggregates (polymolecular micelle); (3–5) successive regular and periodic structures (*i.e.*, spheres, cylinders, lamellaes).

---

(1) M. Szwarc, *Nature (London)*, **178**, 5557 (1956).

(2) M. Szwarc, *Makromol. Chem.*, **35**, 132 (1970).

(3) A. Skoulios, G. Finaz, and J. Parrod, *C. R. Acad. Sci.*, **251**, 739 (1960).

(4) A. Skoulios and G. Finaz, *ibid.*, **252**, 3467 (1961).

(5) (a) B. Gallot, R. Mayer, and Ch. Sadron, *ibid.*, **263**, 42 (1966); (b) *ibid.*, **267**, 1292 (1968).

(6) (a) A. Douy, R. Mayer, J. Rossi, and B. Gallot, Second International Liquid Crystal Conference, Kent, Ohio, Aug 1968; *Mol. Cryst. Liq. Cryst.*, 7, 103 (1969); (b) A. Douy and B. Gallot, IUPAC International Symposium on Macromolecules, Leiden, Holland, 1970, Preprint No. I.22, p 99; (c) A. Douy, M. Gervais, and B. Gallot, *C. R. Acad. Sci.*, **270**, 1646 (1970).

(7) P. Grosius, Y. Gallot, and A. Skoulios, *Makromol. Chem.*, **132**, 35 (1970).

(8) Ch. Sadron, *Pure Appl. Chem.*, **4**, 1347 (1962).

(9) The only theoretical treatment that we know of for AB–S systems has been given by T. Inoue, T. Soen, T. Hashimoto, and M. Kawai, *J. Polym. Sci., Part A-2*, 7, 1293 (1969).

(10) Other theoretical treatments, though relevant to this subject, concern the limiting case of the structure of pure (A, B) systems, that is, (A, B)–S systems where the concentration of S is zero: D. J. Meier, *ibid., Part C*, No. 26, 81 (1969); S. Krause, *ibid., Part A-2*, 7, 249 (1969); *Macromolecules*, 3, 84 (1970).