Note to the Editor

Evidence for the random-coupling structure of an anionically prepared block copolymer

Mitsuru Omoto, Takeshi Tanaka, Satoru Kadokura, and Hiroshi Inagaki
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

(Received 31 July 1978)

A general analysis of the composition and molecular weight distribution of block and graft copolymers is difficult since experimental information is limited. Several authors[1–6] have pointed out that the analysis may be simplified by introducing the hypothesis that the molecular weights of the individual subchains are not correlated, or that the copolymer has a structure characterized by random-coupling or random-grafting statistics. In the light scattering[7] and neutron scattering[8] studies on block copolymer conformation, the hypothesis has formed an essential basis of data analysis.

This hypothesis of independent molecular weights or random coupling appears quite plausible for those block copolymers prepared by an anionic living polymerization method *via* a sequential addition procedure. There have been indirect observations which indicated the random-coupling nature of such block copolymers[2,9,10].

In order to verify the theory, we have chosen polybutadiene (PB)–polystyrene (PS) diblock copolymer as a model system, which is suitable since, firstly two living PB's of widely differing lengths are anionically prepared separately. Secondly, they are mixed, and the second monomer styrene is introduced to form a PB–PS block copolymer. The product will be a mixture of two copolymers largely different in composition, so that they will be easily separated from each other (the third step). In the fourth step, each fraction is subjected to selective degradation of the PB block. Finally, the two PS blocks recovered are compared by using gel permeation chromatography (g.p.c.) for example. If the above hypothesis is true, they should give an identical chromatogram.

Sample preparation was made according to the procedure now routine in our laboratory[5,11]. A small amount of butadiene in benzene solution was reacted with sec-butyllithium to form living polybutadiene (PB_1) with a molecular weight about 4×10^3. The solution was divided into two portions I and II. To I, a large amount of butadiene was introduced, and a sufficient time (66 h) was allowed to complete the reaction. This gave a living PB (PB_2) with a molecular weight about 3.0×10^5 (the g.p.c. pattern of PB_2 is given in *Figure 1a*). Subsequently, PB_1 in II was mixed with PB_2 in I, and a greater portion of the solvent benzene was distilled out of the system. This effected complete removal of butadiene monomer which would have been still present in a small amount due to the low polymerization rate of this monomer, and might have resulted in undesired 'tapered' structures in the PS block. After a sufficient amount of the solvent was newly introduced, styrene monomer was reacted with the living PB's. The reaction was terminated by a trace of methanol. This gave a mixture of two PB–PS block copolymers, the one (BS_1) with (calculated) styrene content of 99% (by wt) and the other (BS_2) of 42%. The g.p.c. pattern of the product is shown in *Figure 1b*. Clearly, the peak at a higher elution count corresponds to BS_1, and the one at a lower count to BS_2.

The crude product was immersed in diethyl malonate (DEM) which is a theta solvent for PS and a non-solvent for PB. The system was kept at a temperature of 50°C for 6 h with gentle stirring. The soluble and insoluble fractions

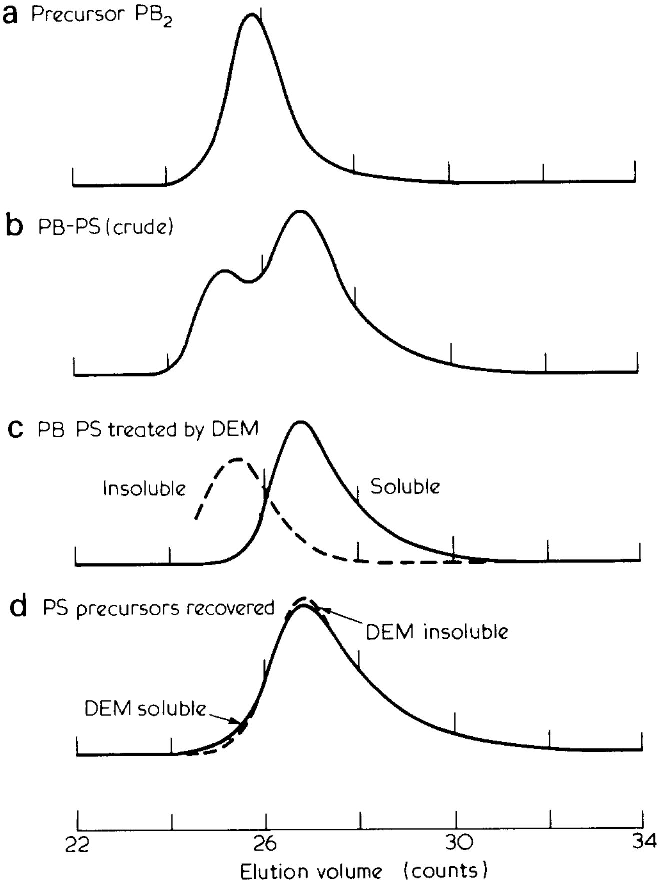

Figure 1 G.p.c. elution patterns for precursor PB_2: (a) crude block copolymer PB–PS (b) DEM-soluble and insoluble fraction (c) and precursor PS's recovered after selective degradation of the PB blocks (d)

0032–3861/79/010129–02$02.00

were separated by filtration. The g.p.c. patterns of the two fractions are given in *Figure 1c*. By comparison of these with *Figure 1b*, it is clear that the soluble and insoluble fractions consist predominantly of BS_1 and BS_2, respectively. (The weight ratio of the two fractions recovered was somewhat different from that of BS_1 and BS_2 calculated from the kinetics. It seems that about 10% of BS_2 went to the soluble fraction. So far as the present problem is concerned, this much of discrepancy should not be taken seriously.)

Each fraction was subjected to oxidative degradation of PB. The method employed was essentially the same as that of Corbin and Prud'homme[12] who used *m*-chloroperbenzoic acid and subsequently periodic acid. It is noticed that unless care is taken, the reaction with the acid causes some degradation of PS as well. Suitable conditions were determined by independent experiments[13]. Composition analysis showed that the polymers recovered after the degradation reaction are pure polystyrenes. Their g.p.c. curves are given in *Figure 1d*. The two curves coincide with each other almost perfectly. The very small discrepancy seen in a high molecular weight region is presumably due to the imperfect separation of BS_1 and BS_2 as indicated above: the DEM-soluble components of BS_2 would be relatively high in styrene content, and hence have longer-than-average PS blocks. In any case, the discrepancy is trivial.

The above result shows that despite the large molecular weight difference between the PB blocks (about a factor of 100), the molecular weight distributions of the PS blocks are the same. This verified the random coupling nature of this block copolymer.

In a two-step block-copolymerization, the molecular weight of the second block should be governed by the crossover reaction and propagation rate constants k_{12} and k_{22}, respectively, and the concentration of the second monomer *around the active polymer end*. No doubt, the first two factors will be independent of the length of the first block (if it is sufficiently long). Likewise we can hardly envisage that the third factor can differ significantly depending on the length of the first block, unless we are concerned with an inhomogeneous system where, for example, one of the two blocks is insoluble. The present result has confirmed this point, and it cannot be the feature particular to PB–PS copolymers.

It should be noted that the present result has nothing to do with the block copolymers obtained by a coupling reaction itself. In certain cases, these polymers can have structure not governed by random-coupling statistics, since the rate constant of the coupling reaction can be a sensitive function of molecular weights.

Another important implication of the present experiments is the possibility of accurate characterization of polydiene block copolymers such as PB–PS and polyisoprene (PI–PS). Following a similar procedure, it is possible to obtain the precursors of the second block (PS) as well as of the first block (PB or PI), and thus their molecular weight distributions can be precisely determined by established methods. The distributions of the two blocks and their average composition are the only factors that specify the compositions and molecular weight distribution function of a 'randomly coupled' block copolymer[6]. In principle, this method could be applied to any block copolymer, if a short polydiene sequence is introduced as an intermediate block.

REFERENCES

1 Leng, M. and Benoit, H. *J. Polym. Sci.* 1962, **57**, 263
2 Freyss, D., Rempp, P. and Benoit, H. *J. Polym. Sci. (B)* 1964, **2**, 217
3 Cordier, P. *J. Chim, Phys.* 1967, **64**, 423
4 Vorlicek, J. and Kratochivil, P. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 855, 1251
5 Ohnuma, H., Kotaka, T. and Inagaki, H. *Polymer* 1969, **10**, 501
6 Kotaka, T., Donkai, N. and Min, T. I. *Bull. Inst. Chem. Res. Kyoto Univ.* 1974, **52**, 332
7 Tanaka, T., Omoto, M. and Inagaki, H. *Polym. Prepr. Jpn* 1977, **26**, 1188; submitted to *Macromolecules*
8 Benoit, H., Lecture at the IUPAC Congress, 5EI=13, Tokyo, 1977; Ionescu, M., *PhD Dissertation*, University of Strasbourg, 1976
9 Kotaka, T., Uda, T., Tanaka, T. and Inagaki, H. *Makromol. Chem.* 1975, **176**, 1273
10 Inagaki, H., Kotaka, T. and Min, T. I. *Pure & Appl. Chem.* 1976, **46**, 61
11 Tanaka, T., Kotaka, T. and Inagaki, H. *Macromolecules* 1974, **7**, 313
12 Corbin, N. and Prud'homme, J. *J. Polym. Sci. (Polym. Chem. Edn)* 1976, **14**, 1649
13 Kadokura, S., Tanaka, T. and Inagaki, H. submitted for publication