

Fractionation of Block Copolymer Methyl Methacrylate—Styrene Obtained by Copolymerization Method

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Basic knowledge on the formation of block copolymer methyl methacrylate—styrene by the reaction of polymethyl methacrylate with unstable bonded fragments of the initiator on the chain ends of basic polymethyl methacrylate with styrene has been obtained by fractionation. In the reaction, no free polystyrene arises practically, in copolymerization reaction, however, one part of polymethyl methacrylate chains is inactive remaining as homopolymer in the reaction mixture.

In the preceding paper [1] a new method of block copolymer methyl methacrylate—styrene was described consisting in utilization of unstable bonded fragments of the initiator at the ends of methyl methacrylate polymer chains for initiation of copolymerization reaction in presence of styrene. In view of the reaction mechanism, the formation of the block copolymer type A—B is assumed.

Copolymer formed in this way is indicated by the results of gas chromatographical analysis of copolymerization products summarized in paper [1]. We, therefore, found it desirable to determine, following to the copolymerization reaction, more precisely the composition of the polymer product in view of the presence of methyl methacrylate, styrene homopolymers and copolymer. To separate copolymer from the reaction mixture, we used the method of selective fractionation by benzene—methanol system. *Burnett et al.* [2] found that, in this system, in the course of precipitation, polystyrene is fractionated first followed by block copolymer and finally, by polymethyl methacrylate. When compared with the extraction by selective solvents (used for the given copolymer *e.g.* in paper [3]), the referred process has the advantage of enabling a more precise determination of polymer admixtures in the reaction mixture (their inclusion into copolymers is less dangerous) providing also a certain picture of polydispersity of the copolymer obtained.

Experimental

Preparation of polymethyl methacrylate with unstable fragments

The polymethyl methacrylate (PMMA) was prepared by polymerization of methyl methacrylate in the presence of 0.2 weight % of 3,3,4,4-tetraphenylhexane at 60°C [1]. Following to half an hour's polymerization, the reaction was interrupted. The polymerization mixture was dissolved in benzene and polymethyl methacrylate was isolated by its precipitation by methanol in nitrogen atmosphere. The polymer was dried in vacuum at room temperature for about 20 hours. The overall weight of the polymer corresponded

to 27.7% conversion. Average molecular weight M_w of the polymer obtained (2.01×10^5) was determined from the value of the intrinsic viscosity number in toluene at 25°C according to the relation $[\eta] = 7.1 \times 10^{-3} \times M_w^{0.73}$ [4].

Preparation of the block copolymer methyl methacrylate—styrene

7 g of polymethyl methacrylate referred to, dissolved in 50 ml of styrene was copolymerized in a sealed glass ampule in nitrogen atmosphere at 80°C, the first sample for as long as 3 and the second for as long as 10 hours. The polymer products of copolymerization were isolated in quite a similar way as in the case of polymethyl methacrylate. The first sample contained 27, the second 41 weight % of styrene.

Block copolymer fractionation

The first sample was fractionated by the current method of fractionation precipitation in the apparatus described by Allen [5]. Methanol was added at 25°C in small amounts to 0.5% benzene solution of copolymer under mixing until turbidity has been formed. Thereafter, the solution was first heated until the turbidity has disappeared, then recooled down to 25°C and after 24 hours of phase equilibrium stabilization, the fraction was taken.

Very often, there would arise, however, a very stable lactic turbidity, the separation occurring very slowly. The coacervate could only be taken after elapse of several days, the time necessary for fractionation being thus unproportionally prolonged.

Hence, the other sample of higher conversion was fractionated by column precipitation chromatography [6] again in benzene—methanol system, the polymer weight being about 5 g. The temperature cycles lasted about 30 minutes over the range of 25—40°C. Limiting composition of eluent in the containers was determined by turbidimetric titration of 1% solution. The column flow rate of eluent was about 100 ml/hr.

The fractions taken were concentrated in vacuum, then precipitated by methanol and dried in vacuum at 60°C up to constant weight. Chemical composition of fractions was determined by pyrolytic gas chromatography [7].

Results and Discussion

The results of both fractionations are shown in Table 1 and 2, respectively, where fraction weights and their chemical composition are expressed by weight fraction of x_{PS} polystyrene (PS). Cumulative weight fraction of I_n fractions is defined

$$I_n = \sum_{i=1}^{n-1} w_i + \frac{w_n}{2} \quad (1)$$

where w_i is the weight fraction of the i -th fraction. Fractionation results of the both samples are shown in Fig. 1 expressing the weight fraction of x_{PS} polystyrene in dependence of I_n cumulative weight.

As we may see, both reaction mixtures contain a relatively considerable amount of PMMA homopolymer. The separation of this homopolymer from copolymer in the course of fractionation is very effective as may be seen from the distribution curves plotted on Fig. 1. In sample 2, the separation is a more perfect one partly because of the greater difference in chemical composition (and hence in molecular

weight as well) of the copolymer, partly because of the application of the more effective fractionation technique, though the influence of higher composition polydispersity of sample 1 on the results obtained cannot be excluded.

On the basis of the referred distribution curves it is, however, not possible to evaluate unambiguously the presence of PS homopolymer in the reaction mix-

Table 1
Fractionation results of sample 1

Number of fraction	Fraction weight [g]	I_n	x_{PS}
1	0.131	0.007	0.63
2	0.572	0.044	0.72
3	0.361	0.093	0.71
4	0.308	0.128	0.67
5	0.173	0.153	0.69
6	0.155	0.170	0.62
7	0.910	0.227	0.61
8	1.202	0.338	0.34
9	1.061	0.457	0.14
10	1.080	0.569	0.08
11	1.124	0.685	0.02
12	1.589	0.828	0.00
13	0.830	0.956	0.00

Losses 4.7%.

Table 2
Fractionation results of sample 2

Number of fraction	Fraction weight [g]	I_n	x_{PS}	$[\eta]$ [ml/g]
1	0.548	0.059	0.02	—
2	0.320	0.152	0.01	77
3	0.614	0.252	0.01	—
4	0.657	0.388	0.01	80
5	0.063	0.465	0.01	—
6	0.082	0.481	0.01	—
7	0.030	0.493	0.09	—
8	0.064	0.503	0.05	—
9	0.063	0.516	0.04	—
10	0.289	0.554	0.06	—
11	1.007	0.693	0.89	141
12	0.527	0.857	0.92	215
13	0.244	0.940	0.92	202
14	0.077	0.975	0.87	230
15	0.014	0.985	0.84	—
16	0.046	0.991	0.78	246
17	0.018	0.998	0.80	—

Losses 4.2%.

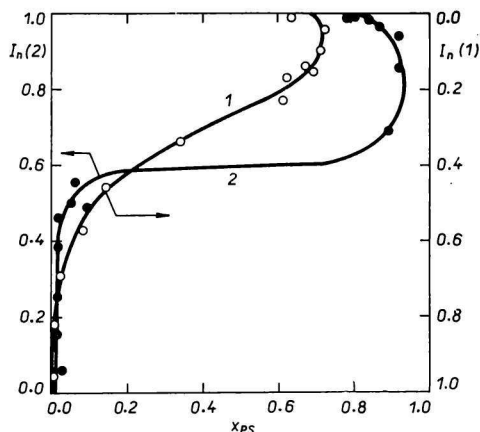


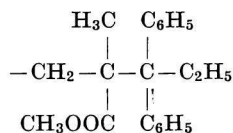
Fig. 1. Distribution curve of chemical composition of sample 1 (○) and sample 2 (●).

ture because, against the effect of the macromolecule separation according to chemical composition, there acts also the effect of their molecular weight (we presume the molecular weight of the copolymer to be higher than that of PS homopolymer). It might be assumed that along with higher molecular weights of copolymer, PS of lower molecular weight is fractionated and hence, its separation does not occur. This presumption, however, appears to be opposed with the results of *Burnett et al.* [2] showing that the effect of chemical composition on methyl methacrylate—styrene copolymer solubility in benzene—methanol system is by far more important than the effect of molecular weight, particularly within the range of higher x_{PS} values. Should the free PS molecular weight compensate the effect of copolymer chemical composition so as to make their solubilities equal to each other, it would have to be considerably lower with respect to that of the copolymer. Since the PMMA contribution to molecular weight of copolymer is, however, relatively small, the molecular weight of free PS would have to be lower than that of copolymer bonded free PS.

From Fig. 1 there may be seen that, should the homopolymer PS be arising in copolymerization, its fractionation would have to proceed in sample 2 already in the region $I_n = 0.7-0.9$, to which pertains volume fraction of precipitant in elution mixture $\gamma = 0.39-0.33$. As shown by the results of turbidimetric measurements, made under given conditions [8], this region corresponds, however, to PS fractionation region of a molecular weight under 1.5×10^5 . Should the copolymerization give rise to PS homopolymer of this molecular weight, there would not be possible to separate it from the copolymer by the above-mentioned fractionation processes. There is, however, a little probability that there could, apart from the copolymerization reaction, arise a PS homopolymer of that low molecular weight. In view of both the molecular weight of the starting PMMA and the chemical composition of the copolymer, a manifold higher copolymer bonded PS molecular weight may well be expected even in the case that in the copolymerization reaction there preferably participated the low-molecular PMMA part as we do consider further on. This is confirmed also by the measured intrinsic viscosity numbers of copolymer fractions in toluene. This possibility can, however, not completely be excluded.

The results may further suggest a relatively low composition polydispersity of copolymers obtained.

From Fig. 1 there may further be seen that with growing conversion degree there increases also styrene content in the copolymer without a remarkable change of the absolute amount of polymethyl methacrylate homopolymer in copolymerization mixture (50% of the original polymethyl methacrylate approximately). There results therefrom that not all polymer chains of the methyl methacrylate are active in copolymer reaction. Despite the evidence that this is also connected with the conditions of sample preparation and that the share of the inactive polymer will change along with them, it may be suggested that in the methyl methacrylate preparation there occurs a certain inactivation of initiation centres at the ends of polymer chains (arising by attaching the fragment of 3,3,4,4-tetraphenylhexane in the termination reaction with polymer radical) of a structure



By comparison of the molecular weights of methyl methacrylate homopolymer fractions (*e.g.* in the second fractionation the second fraction $M_w = 3.38 \times 10^5$ and the fourth fraction $M_w = 3.54 \times 10^5$) with that of the starting polymethyl methacrylate, used in copolymerization ($M_w = 2.01 \times 10^5$) we may see that the methyl methacrylate homopolymer left behind in copolymerization mixture without participating in copolymerization reaction belongs to a part of the original polymer of higher molecular weight. This result corresponds to the notion that in methyl methacrylate polymerization, there is a greater presumption of the loss of initiation centre at the end of the polymer chain of a higher molecular weight than of the lower. At higher M_w , there occurs also a greater amount of splittings and attaching of the initiator fragment to polymer molecule, whereas there is a greater probability that, apart from combination reactions (between polymer radical and initiator fragment) also other reactions leading to polymer chain end inactivation make themselves useful.

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