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COPOLYMERIZATION ON MATRICES

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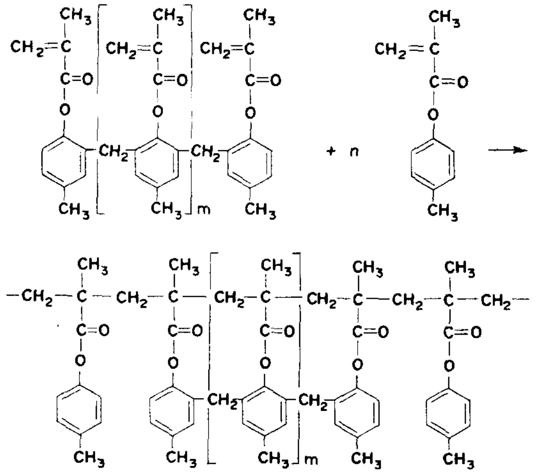
Abstract—By copolymerization of polyfunctional monomers (multimethacrylates) with styrene or *p*-cresyl methacrylate, copolymers containing ladder-type blocks were obtained. Fractionation of the products was carried out; molecular masses, intrinsic viscosities as well as the number of end-groups per polymer molecule were determined. It has been found that these copolymers are only slightly branched; however more than 90% of multimethacrylate units react along the matrix (*p*-cresol-formaldehyde resin).

INTRODUCTION

There have been a few papers dealing with homopolymerization of vinyl monomers on matrices. It has been found that the ordering of monomer molecules by means of covalent bonds [1], hydrogen bridges [2] or van der Waals forces [3] affects the rate of polymerization and the structure of the resulting polymer. It seems that the application of matrices in a copolymerization might influence the distribution of monomer units along the chain. Previous papers [4,5] dealt with the case where the molecules of one of the monomers involved in copolymerization were linked to the matrix by covalent bonds. It was found that, when the number of monomer molecules linked with the matrix was changed, reactivity ratios also changed.

The present paper refers to further investigations concerning copolymerization of multimethacrylates (methacrylate monomer units linked with *p*-cresol-formaldehyde matrix) with styrene or *p*-cresyl methacrylate. The structures of the products were also examined. From the previous papers, it was expected that copolymerization would occur according to the following scheme if *p*-cresyl methacrylate were used as the monomer not linked with the matrix:



In the product, there should be ladder-type blocks linked by means of segments composed of styrene or *p*-cresyl methacrylate monomer units.

EXPERIMENTAL

I. *Synthesis of multimethacrylate*

Synthesis of multimethacrylate was carried out as described previously [4,5]. *p*-Cresol-formaldehyde resin, obtained by polycondensation of *p*-cresol with formaldehyde, was fractionated using acetone/methyl alcohol and water/methyl alcohol. Some fractions were esterified by methacryloyl chloride according to the previous method [4]. The product was again fractionated by precipitation in the system ethyl alcohol/water. For further experiments, 3 fractions were chosen with molecular masses measured cryoscopically of 1619, 1739 and 1860 respectively. Spectrophotometric analyses of the products were carried out by comparing the intensities of the band due to vinyl groups ($1640\,cm^{-1}$) with *p*-cresyl methacrylate used as standard. Full esterification of -OH groups was found in the products.

II. *Synthesis of copolymers*

Sample A. 2.5 g of the matrix (multimethacrylate with molecular mass 1860) with 50 g of styrene and 50 ml of benzene were placed in a flask and flushed for 30 min with purified nitrogen with stirring. AIBN labelled in the CH_3 groups with carbon-14 was added; the specific activity of AIBN was 0.1417 Ci/mole. The flask was heated at 80° for 7 hr. The product was then precipitated by isopropyl alcohol. The crude product was purified by several precipitations from chloroform solution, first with isopropyl alcohol and then with methyl alcohol. After drying in vacuum, 12.5 g of copolymer were obtained.

Sample B. 5 g of multimethacrylate (molecular mass 1619) were copolymerized with 10 g of *p*-cresol methacrylate labelled with tritium. Copolymerization was initiated by unlabelled AIBN. Procedures for copolymerization and purification were as for Sample A.

Sample C. The synthesis was performed as for Sample B, but with 9.3 g of multimethacrylate and 9.3 g of *p*-cresyl methacrylate labelled with tritium. 6.05 g of copolymer were obtained.

Sample D. 1 g of multimethacrylate (molecular mass 1739) and 10 g of *p*-cresol methacrylate were used in 90 ml of benzene. The copolymerization was initiated by ^{14}C-AIBN having specific activity of 0.03264 Ci/mole. The other copolymerization conditions were as for Sample A. 5.56 g of copolymer were obtained.

Fractionation and analysis. For fractionation, fractional precipitation was applied using methyl alcohol with 3% benzene solution of polymer. In view of possible pollution, the small first and last fractions were rejected. From i.r. analysis of fractions (Fig. 1), it was found that double

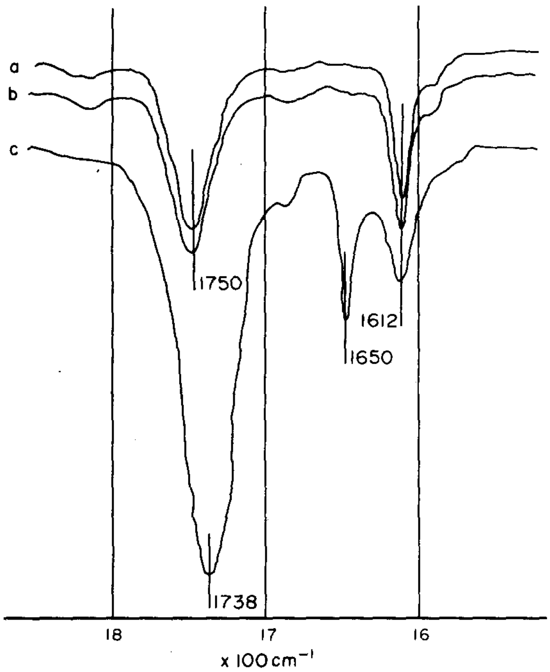


Fig. 1. i.r. Spectrum of sample A and multimethacrylate. a—Sample A fraction 4, b—Sample A fraction 2, c—multimethacrylate (comonomer).

bonds (1650 cm^{-1} peak) were absent in the product. The compositions of the fractions of Sample A were determined by analysis for C and H. The compositions of the fractions from Samples B and C were determined radiometrically using liquid scintillation USB-2 meter with toluene solutions of the scintillator (4 g of POP and 0.9 g POPOP in 1 l. of toluene). Similarly the activities of the samples labelled with ^{14}C (Samples A and D) were evaluated in order to determine the number of active end-groups per macromolecule. Number-average molecular masses were determined using a Knauer membrane osmometer, with solutions in toluene. Weight-average molecular masses were determined by light scattering (wavelength 546 nm) using "Sofica" apparatus made by Wippler and Scheibling. Toluene solutions were filtered with Millipore GS 0.22 filters. The increment of light refractive index was determined by means of the interferometric method.

Molecular masses were calculated by Zimm's method and, for extrapolations, the least squares procedure was used. Viscometric measurements were made using an Ubbelohde viscometer with toluene at 25°. Results are given in the Tables.

DISCUSSION AND CONCLUSIONS

The data show that macromolecular compounds are obtained as the product of copolymerization. All the products were soluble in benzene, toluene, chloroform and acetone, showing that they are not cross-linked although they may be branched. For Sample A labelled with ^{14}C in the end-groups, the middle fractions were analysed because the first and last fractions might have been contaminated.

To evaluate the degree of branching, the number of end-groups per macromolecule was calculated from the formula [6]:

$$y = M(a_p/a_i)$$

where:

M = molecular mass,
a_p = activity of 1 g of polymer,
a_i = activity of 1 chemical equivalent of the initiator (half of molar activity of AIBN).

The data in Table 1 show that the products are branched. Assuming, as for the polymerization of styrene, that termination occurs by combination, the number of points of branching should be $(y - 2)/2$; in all the fractions, this number is about 10. When the molecular mass and the copolymer composition are known, it is possible to calculate the number of methacrylate units per macromolecule; by comparing this value with the number of branching points, one can calculate the number of units which have reacted along the matrix but have not produced branches. Such estimations, e.g. for fraction 2, indicate that only 2% of methacrylate units produce branches. The remaining 98% reacted along the matrix forming a copolymer with ladder-type blocks as shown in the reaction scheme. This interpretation is, of course, not precise.

In Samples B and C, *p*-cresyl methacrylate units occurred in place of styrene. Because the comonomers have similar chemical structures, the application of labelled *p*-cresyl methacrylate was necessary for determination of the number of units in the blocks. In order to determine the composition (percentage of units not linked with the matrix), synthesis of a homopolymer of *p*-cresyl methacrylate labelled with tritium was performed under similar conditions. Its activity was 141 μCi/g. Comparing the activity of the fractions of copolymers B and C with that value, the compositions presented in Tables 2 and 3 have been calculated. As the differences between compositions of fractions were small, it was possible to construct the graph relating intrinsic viscosity to molecular mass. Figure 2 shows that in both cases there is curvature characteristic of branched polymers, although there is scatter of the points caused by slight difference in composition and a large error in the determination of low intrinsic viscosities.

Table 1. Fractionation of copolymer A

Number of fraction	Wt % of fraction	% O_2	Molar fraction of PS	$[\eta]$	$\bar{M}_w \cdot 10^{-5}$	Activity (μCi/g)	Number of end-groups per macromolecule
1	2.7	10.4	0.54	0.445	—	0.626	—
2	16.6	6.4	0.76	0.340	2.50	0.709	24
3	31.9	4.9	0.82	0.230	2.01	0.826	20
4	20.0	4.6	0.83	0.170	1.07	0.876	16
5	11.0	5.6	0.80	0.130	—	1.016	—
6	16.8	5.9	0.78	0.085	0.47	1.388	12
7	1.0	5.4	0.81	—	—	2.167	—

Table 2. Fractionation of copolymer B

Number of fraction	Mass of fraction (g)	Activity (μCi/g)	% of *p*-cresyl methacrylate monomer units	[η]	$\overline{M}_w \cdot 10^{-5}$
1	0.5624	107	75.9	0.275	2.844
2	0.6369	111	78.7	0.225	1.205
3	0.4694	110	78.0	0.165	1.000
4	0.4572	116	82.3	0.140	0.7518
5	0.5115	112	79.4	0.100	0.5273
6	0.4431	119	84.4	0.065	0.2862

Table 3. Fractionation of copolymer C

Number of fraction	Mass of fraction (g)	Activity (μCi/g)	% of *p*-cresyl methacrylate monomer units	[η]	$\overline{M}_w \cdot 10^{-5}$
1	0.4969	43.4	30.78	0.135	2.619
2	0.5216	44.7	31.70	0.095	1.277
3	0.5155	43.1	30.57	0.080	0.9426
4	0.6246	46.4	32.91	0.065	0.4187
5	0.5831	48.4	34.33	0.045	0.3411
6	0.6337	20.9	14.85	0.035	0.1940

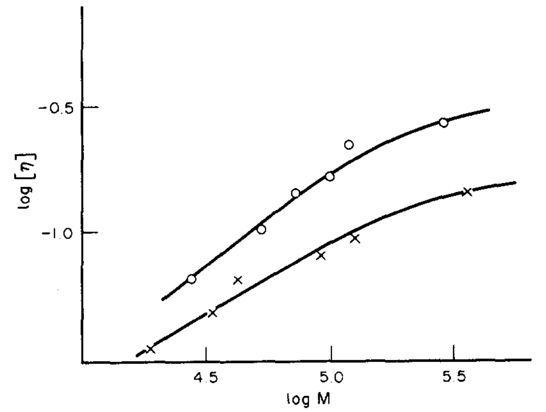


Fig. 2. Intrinsic viscosity as a function of molecular mass: ×—copolymer C; ○—copolymer D.

The analysis of Sample D with ^{14}C-end-groups is presented in Table 4. The calculations of the number of end-groups were carried out as for Sample A. The results show that the number of end-groups per macromolecule is larger in this case, showing a greater degree of branching. For Sample D, it was impossible to estimate the number of monomer units which reacted along the matrix as the composition was unknown. However, one might expect that the change of monomer compared with Sample A would not affect greatly the percentage of conversion along the matrix, taking into account the greater possibility of branching as a result of chain transfer to the polymer.

From the results one can state that, using multimethacrylate as one of the comonomers (i.e. polyfunctional monomer), it is possible to obtain copolymers only slightly branched with ladder-type blocks in the chain. Fractionation of the products shows that solu-

Table 4. Fractionation of copolymer D

Number of fraction	Mass of fraction (g)	Specific activity (μCi/g)	$\overline{M}_n$	Number of end-groups
1	0.6667	8.458	97950	50.8
2	0.1842	8.988	—	—
3	0.3526	8.994	95530	52.7
4	0.1759	9.103	—	—
5	0.2867	9.182	98600	62.1
6	0.1096	9.442	—	—
7	0.4956	9.529	72830	42.6
8	0.4399	9.619	61000	40.3
9	0.1134	9.971	33500	22.9
10	0.1913	10.13	—	—
11	0.3435	10.83	33500	24.9
12	0.3476	11.09	32000	—
13	0.2494	12.27	—	—
14	0.3578	13.18	21400	19.4
15	0.2243	14.58	—	—

bility of these copolymers probably depends on molecular mass, number of branches and on the number of ladder-type blocks in the macromolecule.

From the results, it is uncertain how the grouping of units into ladder-type blocks affects properties of a polymer; this subject will be referred to in a later paper.

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