Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Radiometric Studies on Copolymerization of Multimethacrylate with Styrene

R. Jantas[a]
[a] Institute of Synthetic Fibers Technical University of Łódź, Łódź, Poland

To cite this Article Jantas, R.(1992) 'Radiometric Studies on Copolymerization of Multimethacrylate with Styrene', Journal of Macromolecular Science, Part A, 29: 7, 557 — 566

To link to this Article: DOI: 10.1080/10101329208052182

URL: http://dx.doi.org/10.1080/10101329208052182

J.M.S.—PURE APRL. CHEM., A29(7), pp. 557-566 (1992)

RADIOMETRIC STUDIES ON COPOLYMERIZATION OF MULTIMETHACRYLATE WITH STYRENE

R. JANTAS

Institute of Synthetic Fibers
Technical University of Łódź
90-924 Łódź, Poland

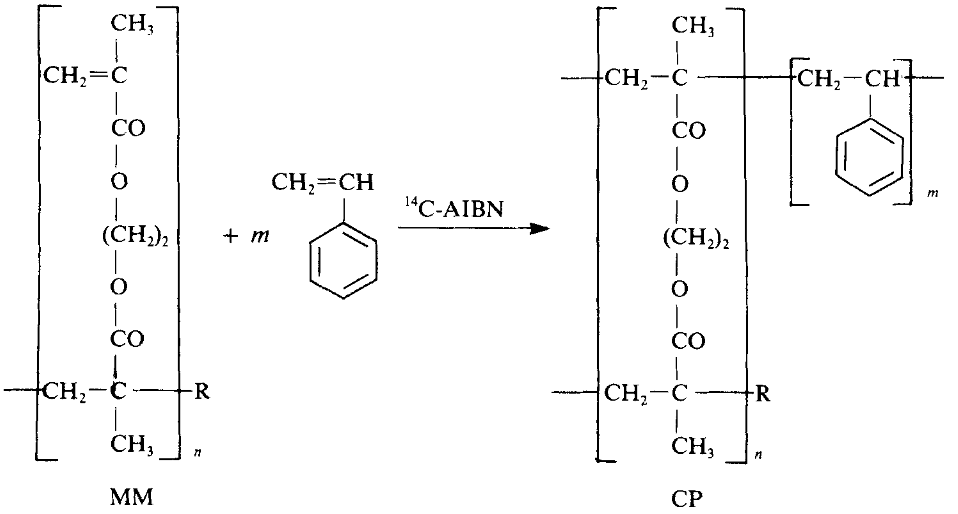
ABSTRACT

Soluble copolymers containing ladder-type blocks are obtained as a result of free-radical copolymerization of a multifunctional monomer (multimethacrylate) with styrene in dilute solutions of DMF. The effects of some conditions of copolymerization on the number of end groups in a macromolecule, number of branching points, molar fraction of methacrylate units which reacted along the template chain, unsaturated residues, copolymer composition, and molecular weight were determined. The results obtained show that more than 80% of methacrylate units reacted along the template chain while the remaining units formed branches or did not participate in the process.

INTRODUCTION

The copolymerization of multifunctional monomers (multimethacrylates) with vinyl monomers has been reported by Połowiński and coworkers [1-6]. In these studies the ordered state of methacrylate units in multimethacrylates was obtained by linking them via covalent bonds with the polymer chain (template). Oligomeric *p*-cresolformaldehyde resin, poly(vinyl alcohol), or polymethacrylate was used as the template. The results of these investigations show that the copolymers obtained by copolymerization of multimonomers with vinyl monomers consist of ladder-type blocks and blocks of vinyl monomer units which are branched and contain unreacted double bonds linked with the template chain.

The present study concerns a further investigation of the copolymerization of multimethacrylate (MM) with styrene in a dilute solution of DMF and examination of the structure of the copolymers by the radiometric method. It follows from our previous study [6] that when styrene is used in the copolymerization as an uncombined monomer, the process should proceed according to the following scheme:



There should be ladder-type blocks linked by means of segments composed of styrene units in the product.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA) was dried and distilled under reduced pressure. Styrene (S) was purified and distilled from CaH_2 under reduced pressure. *N,N*-Dimethylformamide (DMF), tetrahydrofurane (THF), and toluene were dried and distilled under reduced pressure. α,α'-Azobisisobutyronitrile (AIBN), labeled with ^{14}C isotope in methylene groups, was prepared by reacting acetone-1,2-^{14}C with potassium cyanide and hydrazine sulfate [7]. The product was purified by crystallization from methanol. Bromine was dried with concentrated H_2SO_4. Methacrylol chloride was prepared by treating methacrylic acid with thionyl chloride [8]. Poly(2-hydroxyethyl methacrylate) was prepared by the procedure described in Reference 6.

Synthesis of Multimethacrylate (MM)

Multimethacrylate was prepared by Schotten-Baumann esterification of poly(2-hydroxyethyl methacrylate) with methacryloyl chloride. The process was carried out under the optimum conditions described in our previous paper [6]. The MM obtained contained 99.3 mol% of pendant methacrylate groups, showing $\overline{M}_n = 28,230$ ($\overline{P}_n = 142$).

Copolymerization

The copolymerization of MM with S was carried out in a dilute DMF solution under nitrogen in the presence of AIBN labeled with ^{14}C as initiator. When the copolymerization was terminated, the solution was cooled to 0°C and excess bromine was added dropwise. The mixture was heated for 4 h at 35°C. Copolymers were precipitated with methanol, filtered off, and thoroughly washed with warm water and methanol to remove unreacted ^{14}C-initiator and bromine. Purification was accomplished by redissolving in THF and precipitating with heptane. The products were then dried at 30°C in a vacuum dryer to constant weight. This procedure allowed for the preparation of samples with constant specific activities as confirmed in independent experiments.

The copolymer samples were extracted with hot cyclohexane (a solvent for polystyrene), and no soluble fractions were found in the solvent. This confirmed the absence of polystyrene in the products obtained.

Measurements

The number-average molecular weight was determined by the use of a Knauer membrane osmometer in DMF. The composition of MM-S copolymer was determined by spectrophotometry by using the calibration plot of homopolymer mixtures previously prepared. In quantitative analysis, the ratio of the $\rangle C{=}O$ absorption band intensity at 1720 cm^{-1} (characteristic for MM homopolymer) to the $-\overset{|}{\underset{|}{C}}H$ absorption band intensity at 698 cm^{-1} (characteristic for polystyrene) was used. IR spectra of the copolymers under investigation were recorded using 10% solutions in THF. Residual unsaturation (R_{us}) in the copolymers obtained was determined from the bromine content as measured by elemental analysis. Radioactivity of copolymer samples was measured by using a liquid scintillation USB-2 meter.

RESULTS AND DISCUSSION

The results reported in the previous paper [6] showed that the copolymerization of MM with S and acrylonitrile results in soluble copolymers when the process is carried out in dilute DMF solutions (at comonomer concentrations of about 56 g/L) and when bromine is subsequently added to unreacted double bonds linked with the template chain. These copolymers consist partly of ladder-type blocks and partly of blocks of vinyl monomer units which are probably branched.

In order to examine the structure of MM-S copolymers and branch formation in detail, the synthesis was carried out in the presence of AIBN labeled with ^{14}C. The initiator fragments built into the copolymer chain allowed for the determination of the radioactivity of the samples and calculation of the end-group content (N) in a macromolecule of the copolymer from the equation [9]

$$N = \overline{M}_n \, (a_c/a_i) \tag{1}$$

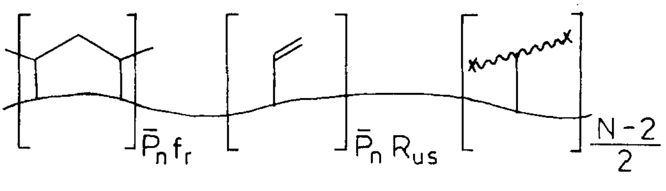
where $\overline{M}_n$ is the number-average molecular weight of the copolymer, a_c is the specific activity of 1 g of copolymer, and a_i is the activity of one chemical equivalent of initiator (a half of the molar AIBN activity).

Assuming (as in the case of styrene polymerization [10, 11]) that the chain termination proceeds through recombination, the number of branching points in a macromolecule was calculated from the relation $(N - 2)/2$.

To calculate the molar fraction of methacrylate units (f_r) which reacted along the template chain without branching, we have derived Eq. (3), assuming that for each macromolecule of the copolymer containing $\bar{P}_n$ methacrylate units there are:

$\bar{P}_n f_r$ units formed by intramolecular reaction of methacrylate double bonds along the template chain.
$\bar{P}_n R_{us}$ methacrylate double bonds which did not react in copolymerization.
$(N - 2)/2$ units formed by intermolecular reaction of double bonds of methacrylate for which it was assumed that each branch unit additionally contains two end-groups.

The above consideration is illustrated by the following scheme:



Hence, the following equation was obtained:

$$\bar{P}_n = \bar{P}_n f_r + \bar{P}_n R_{us} + \frac{N - 2}{2} \tag{2}$$

Therefore:

$$f_r = 1 - R_{us} - \left(\frac{N - 2}{2}\right)\frac{1}{\bar{P}_n} \tag{3}$$

where R_{us} is the residual unsaturation in the copolymer, and N is the number of end groups per copolymer macromolecule. $\bar{P}_n$ was calculated as $\bar{M}_n f_w/198.15$, where $\bar{M}_n$ is the number-average molecular weight of the copolymer, f_w is the weight fraction of methacrylate units in the copolymer, and 198.15 is the molecular weight of the methacrylate unit (ethylene dimethacrylate).

If one assumes termination not by recombination but mainly by disproportionation, as in the case of methyl methacrylate [12, 13], the number of branch points in a macromolecule should be $N - 1$. However, this would not substantially change the value of the molar fraction of methacrylate units reacted along the template chain.

In the MM-S copolymerization under investigation, chain termination probably proceeds by both template termination and cross-termination [14]. However, it is not possible to estimate the relative proportion of the former to the latter from the results obtained.

Tables 1-4 contain the results of the determination of the effects of reaction time, initial composition of comonomer mixture, initiator concentration, and dilution of the reaction system on the copolymerization of MM with S. The data obtained show that the number of end groups and the number of branching points in a macromolecule of the copolymer are affected to the greatest extent by the

TABLE 1. The Effect of Reaction Time on the Copolymerization of MM with S[a]

		Copolymer						
Sample	Reaction time, min	MM, mol%	Bromine content, %	R_{us}[b]	Specific activity, μCi/g	$\overline{M}_n \times 10^{-4}$	N[c]	f_r[d]
CP-1	30	75.92	9.82	0.29	2.89	11.6	10.7	0.70
CP-2	90	48.21	5.14	0.23	5.21	9.8	16.5	0.75
CP-3	180	44.67	3.13	0.15	5.26	9.4	16.0	0.83
CP-4	330	42.84	1.93	0.10	4.79	9.5	14.7	0.88

[a] Reaction conditions: [MM][e] = 0.0483 mol/L; [S] = 0.2101 mol/L; [^{14}C-AIBN][f] = 3.45×10^{-3} mol/L; DMF; 90°C.

[b] Residual unsaturation expressed as the molar ratio of the unreacted pendant groups to the total methacrylate groups linked with the template chain in the copolymer.

[c] Number of end groups per macromolecule.

[d] Molar fraction of methacrylate units reacted along the template chain.

[e] MM calculated per ethylene dimethacrylate unit.

[f] Specific activity of ^{14}C-AIBN = 0.063 Ci/mol.

TABLE 2. The Effect of Initial Composition of the Monomer Mixture MM and S on Their Copolymerization[a]

	Monomer feed			Copolymer						
Sample	[MM], mol/L	[S], mol/L	MM, mol%	MM, mol%	Bromine content, %	R_{us}	Specific activity, μCi/g	$\overline{M}_n \times 10^{-4}$	N	f_r
CP-5	0.0151	0.2878	5.17	23.50	1.25	0.12	0.4256	5.2	15.1	0.82
CP-6	0.0463	0.2047	18.45	45.75	3.25	0.15	0.2334	9.4	14.9	0.83
CP-7	0.0763	0.1452	34.45	58.30	3.35	0.13	0.1298	11.9	10.4	0.86
CP-8	0.1236	0.0688	67.76	81.40	5.81	0.16	0.0752	13.7	6.9	0.84

[a] Reaction conditions: [^{14}C-AIBN][b] = 3.19×10^{-3} mol/L; DMF 90°C; 5.5 h.

[b] Specific activity of ^{14}C-AIBN = 2.974×10^{-3} Ci/mol.

TABLE 3. The Effect of the Concentration of ^{14}C-AIBN on the Copolymerization of MM with S[a]

		Copolymer						
Sample	[^{14}C-AIBN] × 10^3,[b] mol/L	MM, mol%	Bromine content, %	R_{us}	Specific activity, μCi/g	$\overline{M}_n \times 10^{-4}$	N	f_r
CP-9	0.89	51.90	4.41	0.19	0.0657	15.8	7.0	0.81
CP-10	4.31	45.90	3.07	0.15	0.2599	9.3	16.2	0.83
CP-11	8.07	36.93	—	—	0.4328	9.1	26.4	—
CP-12	15.95	28.46	0.77	0.06	0.6858	8.9	41.0	0.84

[a] Reaction conditions: [MM] = 0.0463 mol/L; [S] = 0.2047 mol/L; DMF; 90°C; 5.5 h.

[b] Specific activity of ^{14}C-AIBN = 2.974×10^{-3} Ci/mol.

TABLE 4. The Effect of Dilution of the Reaction System on the Copolymerization of MM with S[a]

	Monomer feed				Copolymer						
Sample	[MM], mol/L	[S], mol/L	MM, mol%	$\frac{[^{14}\text{C-AIBN}]}{[\text{MM}] + [\text{S}]} \times 10^3$ [b]	MM, mol%	Bromine content, %	R_{us}	Specific activity, μCi/g	$\overline{M}_n \times 10^{-4}$	N	f_r
CP-13	0.0996	0.1895	34.45	0.0143	55.23	3.45	0.14	0.1932	12.3	16.0	0.84
CP-14	0.0689	0.1307	34.34	0.0136	61.72	3.71	0.13	0.1731	9.7	11.3	0.86
CP-15	0.0523	0.1002	34.29	0.0140	67.45	4.81	0.16	0.1837	8.8	10.8	0.83

[a] Reaction conditions: DMF; 90°C; 5.5 h.

[b] Specific activity of ^{14}C-AIBN = 2.97×10^{-3} Ci/mol.

initiator concentration (Table 3) and to a lesser extent by the initial composition of the comonomer mixture. After 90 min of the process, the number of branching points was almost constant at 7 (Table 1).

The molar fraction of methacrylate units, f_r, which react along the template chain, increases with the reaction time, and after 330 min it reaches 0.88 (Table 1). In a practical sense, the value of f_r does not depend on the initial composition and the dilution of the system. It is in the range from 0.81 to 0.86.

This can be contrasted to the copolymerization of styrene with multimethacrylate linked with the *p*-cresolformaldehyde template, for which Połowiński [3] found that 98% of the multimethacrylate units reacted along the template.

The residual unsaturation in the copolymers decreases with the time of reaction and increases with the initiator concentration, while it increases to a small extent with an increase in MM content in the comonomer mixture and dilution of the system. All the copolymer samples have a higher MM content than that of the initial comonomer mixture.

The number-average molecular weights of the copolymers depend on the initial composition of the comonomers and decrease with an increase in S; they depend to only a small extent on the initiator concentration and the dilution of the reaction system.

CONCLUSIONS

The following conclusions can be drawn from the results obtained:

1. Free-radical copolymerization of MM and S diluted in DMF solution gives a branched copolymer consisting of ladder-type blocks and blocks of styrene units containing unreacted double bonds linked with the template chain.
2. More than 80% of methacrylate double bonds in multimethacrylate react according to the template mechanism to form ladder-type blocks in the product.
3. The number of branches usually ranges from 3 to 7, although there can be up to 20 with a high AIBN concentration.
4. The lack of crosslinking plus the small increase of $\overline{M}_n$ with N implies many short S segments which terminate rather than propagate through a second (or third) MM chain.

ACKNOWLEDGMENTS

The study was partly supported financially by the Polish Academy of Sciences, Research Program 01.14. The author wishes to thank Prof. S. Połowiński for helpful discussions.

REFERENCES

[1] S. Połowiński, *Polimery, 17*, 409 (1972).
[2] S. Połowiński and G. Janowska, *Eur. Polym. J., 11*, 183 (1975).
[3] S. Połowiński, *Ibid., 14*, 563 (1978).

[4] R. Jantas and S. Połowiński, *J. Polym. Sci., Polym. Chem. Ed.*, *24*, 1819 (1986).

[5] R. Jantas and S. Połowiński, *Acta Polym.*, *40*, 225 (1980).

[6] R. Jantas, *Ibid.*, In Press.

[7] A. Murray and D. L. Williams, *Organic Synthesis with Isotopes*, Interscience, New York, 1958, p. 487.

[8] J. A. Arbuzowa, L. J. Medvedeva, and S. P. Plotkina, *Zh. Obshch. Khim.*, *26*, 1127 (1956).

[9] S. Połowiński and W. Reimschüssel, *Polimery*, *10*, 525 (1965).

[10] J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci.*, *14*, 465 (1954).

[11] G. Moad, D. H. Solomon, S. R. Johns, and R. Willing, *Macromolecules*, *17*, 1094 (1984).

[12] P. W. Allen, G. Ayrey, F. M. Merret, and C. G. Moore, *J. Polym. Sci.*, *22*, 549 (1956).

[13] G. Ayrey and C. G. Moore, *Ibid.*, *36*, 41 (1959).

[14] H. T. van de Grampel, Y. Y. Tan, and G. Challa, *Macromolecules*, *24*, 3773 (1991).

Revision received November 28, 1991