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THE STRUCTURE OF COPOLYMERS OF SOME ALKYL METHACRYLATES WITH TRIALLYL CYANURATE

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ABSTRACT

Copolymers of several methacrylates (propyl, pentyl, cyclohexyl and dodecyl) with triallyl cyanurate were synthesized by free-radical polymerization using benzoyl peroxide as an initiator. The structure of copolymers was analysed by quantitative extraction and followed by IR, ^{1}H-NMR and elemental analyses.

INTRODUCTION

The paper presents further results on the free radical copolymers of higher methacrylates with triallyl cyanurate. In preceding papers [2,3] the reactivity ratios of comonomer pairs as well as some properties of copolymers have been reported.

The present paper deals with the synthesis and structure of copolymers of propyl, pentyl, cyclohexyl and dodecyl methacrylathes with triallyl cyanurate. Each copolymer contained 10 and 20 wt% of TAC. The copolymers were obtained by free-radical bulk polymerization with benzoyl peroxide as an initiator. The structure of copolymers was analyzed by quantitative extraction and by IR, ^{1}H-NMR and elemental analyses.

MATERIALS

The monomeric methacrylates: propyl (PrMA), pentyl (PtMA), cyclohexyl (CHxMA), and dodecyl (DdMA) were prepared by transesterification from methyl methacrylate and corresponding alcohols as described elsewhere [4-6]. The purity of monomers was checked by measuring their physical properties (see Table 1) and by IR and ^{1}H-NMR [1-6].

The synthesis of triallyl cyanurate (TAC) was described elsewhere [7]. The nitrogen content was 16.8% as determined by Kieldahl's method (calculated 16.86%), mp 27-28°C , bp 137-140°C n_D^{20} = 1.5060, n_D^{25} = 1.5049.

Benzoyl peroxide (BP), pure grade (Argon, Łódź, Poland), containing 86.5 % of assay [8] was used as supplied.

METHODS

PrMA-TAC, PtMA-TAC, CHxMA-TAC, and DdMA-TAC copolymers were obtained by free radical copolymerization using 0.2 wt% BP as the initiator. Under the same conditions homopolymers of methacrylates and triallyl cyanurate were obtained for reference. Compositions of copolymers are presented in Table 2. The bulk copolymerization was carried out in glass ampules as described previously [2-3]. The nominal content of TAC in each copolymer was about 10 or 20 wt.%.

The extraction of copolymers was carried out in acetone for 50h in the Soxhlet extractor. After extraction the gel was carefully removed from Soxhlet extractor and dried in vacuo on a Petri dish at room temperature to a constant weight. The extract, freed from acetone in a rotary evaporator was dried in vacuo at room temperature to a constant weight. The gel and sol fractions were analyzed by elemental, IR, and ^{1}H-NMR analyses, (^{1}H- NMR for sol only).

IR spectra of copolymers (KBr pellets) were recorded on a SPECORD-71 IR spectrometer (Carl Zeiss Jena, Germany).

Table 1.
Physical Properties of Alkyl Methacrylates

Monomer	Bp (°C) mm Hg	d_4^{20}	n_D^{20}	Molecular Weight		Saponification Number	
				Calcd.	Found*	Calcd.	Found
PrMA	40/80	0.9060	1.4191	128.2	128.6	438	444
PtMA	77/17	0.8913	1.4277	156.0	154.0	359	362
CHxMA	345/5.3	0.9680	1.4581	168.2	176.9	333	332
DdMA	179/14	0.8753	1.4450	254.4	222.2	221	219

* From cryoscopic analysis in dioxane

Table 2.
Composition of copolymers

Sample No	AMA wt.%	TAC wt.%	Numbres of MA per 1 mol of TAC			
			PrMA	PtMA	CHxMA	DdMA
III	95	5	36.7	30.3	28.1	18.6
IV	90	10	17.5	14.4	13.3	8.8
V	85	15	11.0	9.0	8.4	5.6
VI	80	20	7.8	6.4	5.9	3.9

AMA - Alkyl Methacrylate
TAC - Triallyl Cyanurate

^1H-NMR ($CDCl_3$) spectra recorded in ppm (δ units), were obtained with BS 587A spectrometer (Czecho-Slovakia) at the frequency 80 MHz.

The elemental analysis was carried out using EA 1108 Elemental Analyzer (Carlo Erba, Italy).

RESULTS AND DISCUSSION

The scheme of reaction leading to the formation of alkyl methacrylates - triallyl cyanurate copolymers can be presented as follows:

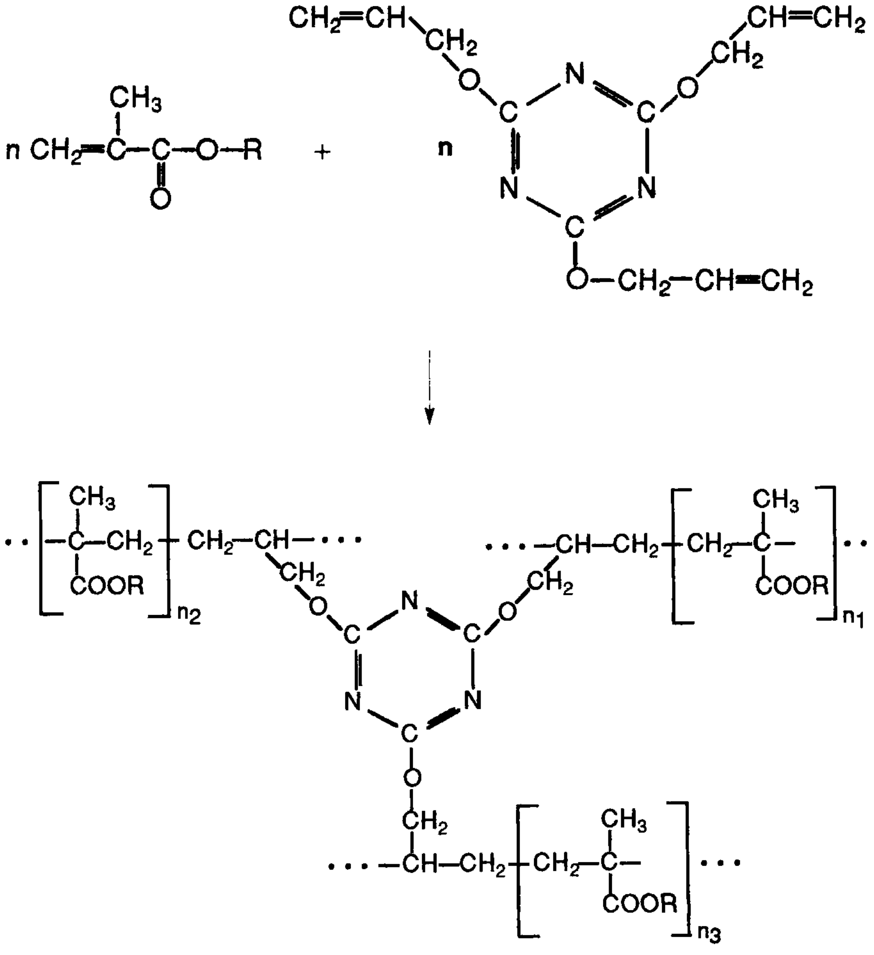

Table 3.

Results of extraction of Alkyl Methacrylate and Triallyl Cyanurate copolymers

Copolymer	Sample No	Gel				Sol	
		Q	U	N* [%]	n	N* [%]	n
PrMA + TAC	I	7.37	96.1	1.64	18	1.28	24
	II	6.23	97.4	3.35	8	1.03	30
PtMA + TAC	I	1.36	94.9	1.48	17	1.03	25
	II	2.36	96.9	3.08	7	1.22	19
CHxMA + TAC	I	6.34	93.4	1.76	13	1.03	23
	II	7.23	95.2	3.48	6	1.12	21
DdMA + TAC	I	6.65	91.1	1.38	11	0.93	17
	II	8.50	92.5	3.73	4	1.05	15

Compositions of copolymers are showed in Table 2.

Q - swelling ratio [%]

U - crosslinked part (gel) [%]

* - average results for two or three measurements

n - number of methacrylate units per TAC unit

where: R = $-C_3H_7$, $-C_5H_{11}$, $-C_6H_{11}$(cyclohexyl), or $-C_{12}H_{25}$

n_1 n_2, n_3 = 0, 1, 2 ....

In copolymerization of triallyl cyanurate with alkyl methacrylates, one, two or all three allyl groups of cyanurate may take part in the copolymerization. The homopolymers of methacrylates or triallyl cyanurate may be formed, too. Important information about the structure

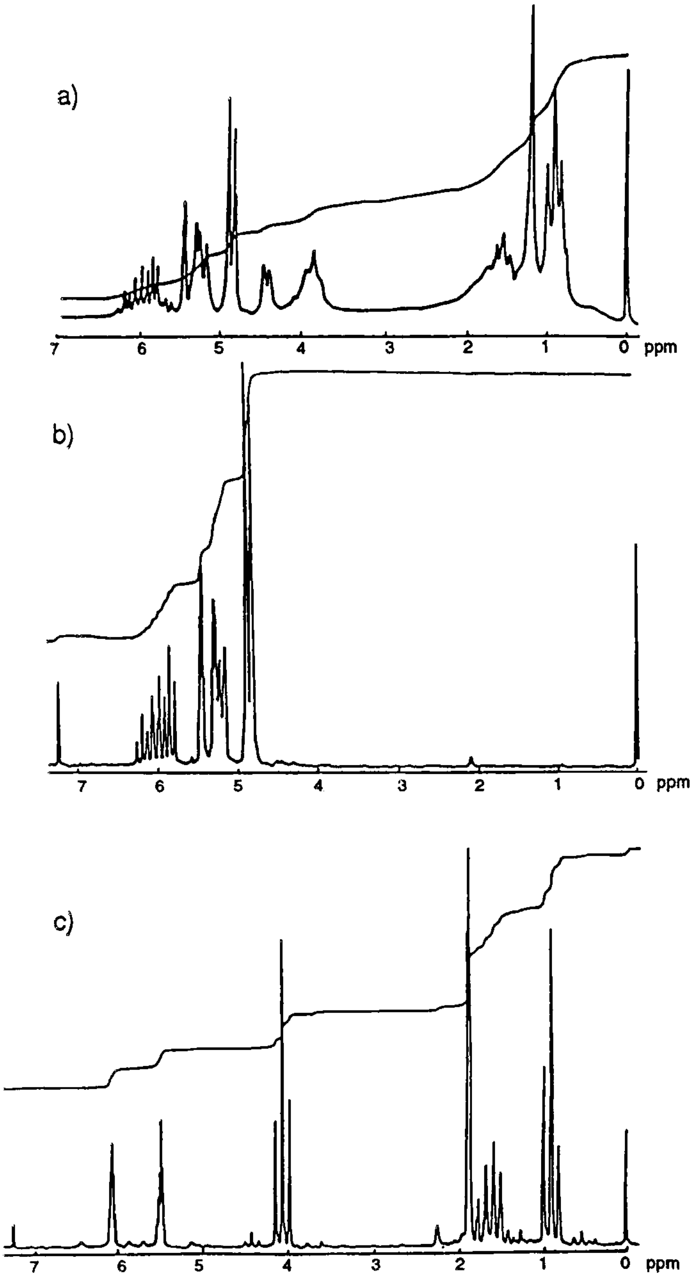

Fig.1. ^{1}H-NMR spectra of : a) Pr-MA, copolymer sol fraction, b) TAC monomer, c) PrMA monomer

of copolymers can be obtained by extraction of copolymer samples in acetone followed by IR, ^{1}H-NMR and elemental analyses of sol and gel fractions. The extraction was carried out to remove soluble fraction of homo- or copolymers. The results of extraction for the systems: PrMA-TAC, PtMA-TAC, CHxMA- TAC, DdMA-TAC (each containing about 10 or 20 wt.% of TAC) are presented in Table 3. The 50h extraction revealed that the content of crosslinked fraction (gel) was above 90 wt.%. The remaining (< 10%) part of the copolymers was soluble in acetone. From the elemental analysis (content of nitrogen) of sol and gel, the number of methacrylate units per one unit of TAC was calculated. The results are presented in Table 3. However, for the same content of TAC in the starting comonomer composition the fraction of methacrylate units in sol is greater than in the gel. This quite expected result was confirmed by ^{1}H-NMR and IR analyses. In the ^{1}H - NMR spectrum of PrMA - TAC sol the signals at 4.88 ppm (dublet), 5.45-5.15 ppm (multiplet) and 6.25-5.77 ppm (multiplet) for allyl groups are clearly seen.

On the other hand, we cannot see any signal at 1.98 ppm for [(C=C(CH$_3$)]. However, appears the signal at 1.22 ppm from aliphatic groups (CH$_2$), which are formation in results of breaking (C=C) double bonds. IR spectra of sol confirm the structure of copolymers. They contain strong bonds of methacrylates at 1730 cm^{-1} (C=O), 1175 cm^{-1} (C-O-C), 1070-1040 cm^{-1} and ca. 720 $(CH_2)_{n>4}$ cm^{-1}, and of s-triazine at 1575 cm^{-1}, 1415 cm^{-1}, and 825 cm^{-1} (C=N) in the ring. No absorption bond for the (C=C) double bonds in the range 1640-1660 cm^{-1} was observed.

CONCLUSION

In the radical bulk copolymerization of alkyl methacrylates (propyl pentyl, cyclohexyl and dodecyl) with triallyl cyanurate, crosslinked copolymers were obtained. However, there was an acetone soluble fraction in the amount below 10%. The composition of sol fraction was confirmed by ^{1}H-NMR, IR, and elemental analyses. This conclusion is consistent with the earlier one based on reactivity ratios [1].

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