

Copolymerization of Hydroxyalkyl Methacrylates with Acrylamide and Methacrylamide. II. Properties of the Copolymers

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ABSTRACT: Copolymers of 2-hydroxyethyl-methacrylate, 2-hydroxypropyl-methacrylate, or 3-chloro-2-hydroxypropyl methacrylate with acrylamide or methacrylamide having different compositions were synthesized by free radical bulk polymerization. Some of their properties, for example, density, polymerization shrinkage, Vicat's softening point, glass transition temperature, hardness, and thermal and chemical stability were measured. The effect of the content of acrylamide or methacrylamide units on the properties of copolymers is discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1243–1248, 1998

Key words: hydroxyalkyl methacrylates; acrylamide; methacrylamide; copolymers; properties

INTRODUCTION

In the radical initiated copolymerization of hydroxyalkyl methacrylates (HEMA), such as 2-hydroxyethyl methacrylate (HAMA), 2-hydroxypropyl methacrylate (HPMA), or 3-chloro-2-hydroxypropyl methacrylate (CHPMA), with acrylamide (AA) or methacrylamide (MA), one obtains (at low conversion) copolymers enriched in respective methacrylate units as compared with comonomer mixtures. The comonomer reactivity ratios¹ indicate that AA or MA units may substantially modify properties of hydroxyalkyl methacrylate polymers. In the present work, we discuss the effect of the content of AA and MA units upon the properties of their copolymers with hydroxyalkyl methacrylates.

EXPERIMENTAL

Monomers

The methods of monomer preparation as well as their properties were described elsewhere.¹

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Polymerization

The monomer mixtures of the compositions listed in Table I (ca. 10 g) were sealed in 25 mL glass ampoules. Benzoyl peroxide (0.5 wt %) was used as an initiator. The ampoules were kept in a thermostat bath with the temperature changed according to the following sequence: 40°C for 2 h, 50°C for 4 h, 60°C for 4 h, 70°C for 4 h, 80°C for 8 h, 90°C for 18 h, and 100°C for 120 h. The temperature was then lowered gradually by 10°C every 5 h. Several ampoules containing the same monomer mixtures were prepared. The polymer was removed from ampoules and cut into samples for further characterization. From the central part of each polymer cylinder, up to five specimens were cut out.

Copolymers Properties

Density and Polymerization Shrinkage

The density of copolymers d_p was measured at 293 K by using a hydrostatic balance with ZnCl₂-water mixtures. The density of comonomer mixtures d_m was measured pycnometrically at the

Table I Some Properties of Copolymers of Hydroxyalkyl Methacrylates (HAMA) and Acrylamide or Methacrylamide

Polymer/ Copolymer	Sample	Comonomer Composition (wt %)		Copolymer Properties				
		HAMA	Amide	Density d_p (g/cm ³)	Shrinkage on Polymn S_c (%)	Glass Trans Temp T_g (°C)	Softening Point (°C)	Hardness (kg/cm ²)
HEMA	—	100	0	1.27	15.49	103.0	88	933
HEMA-AA	1	95	5	1.27	15.37	104.5	89	1330
	2	90	10	1.27	15.22	105.0	89	1333
	3	85	15	1.27	15.43	105.0	90	1333
	4	80	20	1.28	15.48	107.0	92	1300
	5	75	25	1.29	15.94	111.0	95	1233
HEMA-MA	1	95	5	1.27	15.77	106.0	91	1030
	2	90	10	1.27	15.85	108.0	95	1033
	3	85	15	1.27	15.89	111.0	99	1100
	4	80	20	1.28	16.44	114.0	100	1333
	5	75	25	1.29	16.70	117.0	105	1400
HPMA	—	100	0	1.20	14.43	105.0	92	1863
HPMA-AA	1	95	5	1.21	14.58	110.0	97	2010
	2	90	10	1.22	14.78	114.0	101	2070
	3	85	15	1.22	14.83	117.0	100	2100
	4	80	20	1.20	14.82	121.0	98	2060
	5	75	25	1.23	14.67	127.0	100	2360
HPMA-MA	1	95	5	1.20	14.32	111.0	95	1890
	2	90	10	1.20	14.24	117.0	99	1903
	3	85	15	1.21	14.11	123.0	102	1900
	4	80	20	1.21	14.10	128.0	105	1853
	5	75	25	1.21	14.16	133.0	108	1883
CHPMA	—	100	0	1.35	11.03	80	73	1467
CHPMA-AA	1	95	5	1.35	11.85	92.0	76	1650
	2	90	10	1.36	12.34	100.0	80	1700
	3	85	15	1.37	13.34	107.5	85	1500
	4	80	20	1.35	12.61	112.0	87	1433
	5	75	25	1.36	13.60	115.0	90	1333
CHPMA-MA	1	95	5	1.33	10.12	96.0	79	1510
	2	90	10	1.37	13.23	105.0	85	1567
	3	85	15	1.36	13.51	112.0	90	1700
	4	80	20	1.35	13.40	117.0	92	1733
	5	75	25	1.40	16.76	121.0	95	1833

same temperature.^{2,3} The polymerization shrinkage was calculated as

$$S_c = \frac{d_p - d_m}{d_p} \cdot 100 [\%]$$

Vicat's Softening Point

This was measured as the softening point in the Vicat's apparatus.⁴

Glass Transition Temperature

The glass transition temperature was measured on a Perkin-Elmer differential scanning calorim-

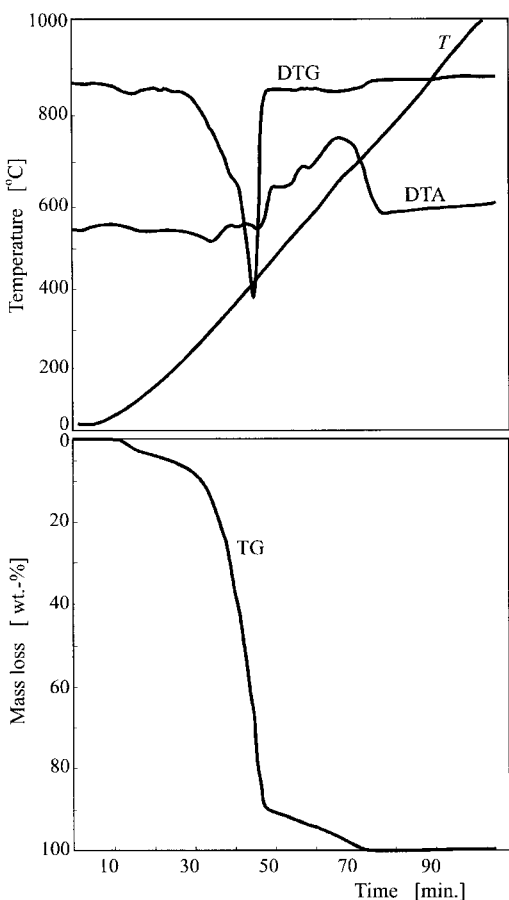
eter DSC-1B. Sample mass was 0.016 g, heating rates were 16, 32, and 64°/min at the temperature range of 40–150°C. Before the actual run, the sample was heated from 40 to 150°C and cooled down to room temperature, both at the rate 4°C min. The glass transition temperatures presented in Table I are those extrapolated to zero heating rate.

Thermal Stability

The thermal analysis of the copolymers was performed using a dynamic method. The measurements were carried out using a Paulik-Paulik-Er-

Table II Thermal Stability of Hydroxyalkyl Methacrylate Polymers and Copolymers

Polymer/ Copolymer	Comonomer Composition (wt %)		Temperature at the Fastest Decomposition (°C)	Temperature at 5% Decomposition (°C)
	HAMA	Amide		
HEMA	100	0	340	190
HEMA-AA	95	5	415	198
	90	10	444	225
	80	20	415	195
HEMA-MA	90	10	420	195
	80	20	360	190
	80	20	280	210
HPMA-AA	95	5	375	220
	90	10	375	200
	80	20	380	200
HPMA-MA	95	5	295	220
	90	10	380	220
	80	20	310, 440	300
CHPMA	100	0	480	180
CHPMA-MA	95	5	430	200
	90	10	435	200
	80	20	310, 440	300



dey derivatograph (Hungary) to obtain differential thermal analysis (DTA), DTG, and thermogravimetric (TG) curves at the following conditions: 20–1000°C temperature range; nitrogen atmosphere; 100 min registration time; 200 mg sample.

Hardness

The hardness of copolymers was measured using the Brinell apparatus.⁴

Chemical Stability

The chemical resistance of the copolymers when immersed in several organic solvents, as well as inorganic acids and bases, was established according to the Polish Standard PN-78/C-89067. The samples of copolymers were immersed into the following media: benzene, chloroform, methanol, 1,4-dioxane, acetone, acetic acid, ethyl acetate, and concentrated or dilute aqueous solutions of hydrochloric, nitric, sulfuric acid, as well as in sodium hydroxide (10 and 40 wt % aqueous solutions). The change of sample mass was measured,

Figure 1 The typical result of thermal analysis with DTA, DTG, TG, and temperature program (T) curves measured for the copolymer of hydroxyethyl methacrylate (95 wt %) with acrylamide (5 wt %).

Table III The Chemical Stability of Hydroxyalkyl Methacrylate Polymers and Their Copolymers with Acrylamide or Methacrylamide Against Inorganic Acids and Bases Expressed as the Increase in Sample Mass (wt %)^b

Comonomers	Sample ^a	30% H ₂ SO ₄	75% H ₂ SO ₄	98% H ₂ SO ₄	10% HNO ₃	40% HNO ₃	10% HCl	30% HCl	40% NaOH
HEMA		17	S ^b	S	13	31	83	121	2.7
HEMA-AA	2	37	S	S	19	62	61	198	S
	3	45	S	S	15	41	60	241	S
	4	83	S	S	13	32	44	203	S
	5	30	S	S	16	27	39	187	S
	2	63	S	S	10	67	19	203	16
HEMA-MA	3	87	S	S	37	33	43	119	39
	4	95	S	S	29	17	33	100	36
	5	68	S	S	15	41	55	161	89
		13	S	S	17	25	23	127	6
HPMA		13	S	S	17	25	23	127	6
HPMA-AA	2	19	S	S	75	55	23	135	17
	3	12	S	S	65	74	45	160	22
	4	19	S	S	57	111	34	139	28
HPMA-MA	2	34	S	S	9	13	16	117	8
	4	90	S	S	8	10	38	118	25
	5	103	S	S	55	6	9	150	132
CHPMA		18	S	S	14	25	43	173	5.3
CHPMA-AA	2	22	S	S	19	41	61	212	S
	3	44	S	S	21	66	74	208	S
	4	16	S	S	16	120	14	219	S
	5	23	S	S	17	80	20	163	S
CHPMA-MA	2	14	S	S	20	44	13	115	9.8
	3	20	S	S	34	56	18	209	21
	4	33	S	S	17	74	23	164	11
	5	41	S	S	21	31	31	171	33

^a See Table I for composition of samples; standard deviation of the results was below $\pm 2\%$.

^b "S" means that sample dissolves or liquifies.

and its appearance was examined after seven days.

RESULTS AND DISCUSSION

The bulk copolymers of hydroxyalkyl methacrylates with acrylamide or methacrylamide are not the pure copolymers like those small conversion ones obtained in our previous work.¹ They were polydisperse in composition. The magnitudes of the comonomer reactivity ratios suggested that the compositions of polymer molecules formed at different conversions must have differed significantly. The amides had the reactivity ratios close to zero.¹ Nevertheless, all bulk copolymers, even those obtained with 25 wt % of acrylamide or methacrylamide, were hard, glassy, and clear products.

The copolymers have been characterized in order to determine their basic physical properties, such as density, polymerization shrinkage, glass transition temperature, softening point, and hardness, as well as their thermal stability. The results are collected in Tables I and II.

It has been noticed that an increase in the content of amide units results in a slight increase of copolymer density, whereas the polymerization shrinkage remains more or less constant. The only exception are the copolymers of 3-chloro-2-hydroxypropyl. For these copolymers, the shrinkage also increases with increasing content of amide units.

The glass transition temperature of the copolymers increases with increasing content of amide units. This dependence seems obvious since, as the polarity of the copolymers increases, the intermolecular interaction strengthens, which results in a reduced mobility of chain segments. It can

Table IV The Chemical Stability of Hydroxyalkyl Methacrylate Polymers and Their Copolymers with Acrylamide or Methacrylamide Against Organic Solvents Expressed as the Increase in Sample Mass (wt %)

Comonomers	Sample ^a	Acetone	Methanol	Dioxane	Chloroform	Benzene	Ethyl Acetate	Acetic Acid
HEMA		20	15	15	16	0.29	4.4	169
HEMA-AA	2	63	40	23	14	0.64	6.7	174
	3	29	17	41	11	-0.31	15	95
	4	29	4.6	41	12	6.4	0.82	85
	5	30	20	32	8.2	2.9	1.5	107
	2	9.6	62	9.6	6.4	0.42	3.5	100
HEMA-MA	3	53	76	22	5.0	1.9	0.67	261
	4	64	49	5.7	2.4	3.3	4.3	321
	5	60	82	3.3	1.1	0.62	0.23	102
	HPMA	17	31	52	36	-1.5	7.2	107
HPMA-AA	2	30	24	57	6.2	1.8	3.1	104
	3	16	19	28	6.8	1.7	2.3	79
	4	2.8	35	2.0	34	4.9	5.8	46
HPMA-MA	2	26	38	43	7.0	0.48	2.5	132
	4	40	38	4.1	0.86	1.6	0.57	304
	5	20	108	0.99	0.32	0.92	0.64	283
CHPMA		31	17	43	17	3.3	17	96
CHPMA-AA	2	26	24	-0.49	19	8.3	1.9	137
	3	49	10	44	15	4.6	9.5	230
	4	13	43	16	20	5.9	8.5	244
	5	20	40	34	14	0.27	0.27	141
CHPMA-MA	2	53	49	9.6	3.3	1.5	5.4	96
	3	50	53	17	4.3	3.8	14	168
	4	103	73	4.9	6.5	4.4	8.6	237
	5	142	16	8.7	8.6	0.29	9.3	303

^a See Table I for composition of samples; standard deviation of the results was below $\pm 2\%$.

be seen well for the copolymers of HPMA and CHPMA.

The composition dependence of the copolymer softening point follows the same pattern as that of the glass transition temperature.

The introduction of amide units into copolymer structures leads to enhanced thermal stability of the products. This again may be caused by the increased polarity and stiffness of copolymer chains.

The hardness of hydroxyalkyl methacrylate copolymers with acrylamide or methacrylamide generally increases with increasing content of amide units. The hardness tends to decrease, however, at above a certain number of these units.

The differential thermal analysis curves (Fig. 1) revealed the presence of several endotherm peaks in the temperature range of 20–1000°C. The first peak at 100–108°C, which is not accompanied by any change of sample mass, corresponds to the glass transition (cf.

DSC results in Table I). The following peaks are due to the thermal decomposition of copolymers. As follows from TG curves, the decomposition starts soon above T_g . A rapid decomposition starts at approximately 400°C and ends at 600–700°C. The thermal stability of the samples are characterized in Table II by the two following parameters: (1) the temperature of the sample's fastest decomposition read out from DTG curve, and (2) the temperature $T_{5\%}$, at which 5% weight loss of the sample has been encountered at TG curve.

The results presented in Table II suggest that introduction of 5–10 wt % of amide units results in a significant increase of thermal stability of the copolymers. A further increase in their content is not that effective anymore. From the point of view of the thermal stability of HAMA copolymers, application of more than 5–10 wt % of acryl- or methacrylamide comonomer becomes impractical.

The chemical stability of the homo- and copoly-

mers was measured for two kinds of aggressive media. The first group consisted of inorganic acids and bases (Table III); the second was the group of typical organic solvents (Table IV).

It was found that the copolymers are sensitive towards strong inorganic acids and bases. The sensitivity is favored by the presence of amide units. A similar effect has the amide units on the resistance of the copolymers against acetone, methanol, and acetic acid. The copolymers seem resistant against benzene, ethyl acetate, and chloroform.

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