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The Copolymerization of Alkylene Glycol Nitrate Acrylates and Methacrylates

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The copolymerization of alkylene glycol nitrate acrylates (ANA) and methacrylates (ANMA) $[M_2]$ with styrene $[M_1]$ has been carried out at 60°C. The alkylene glycol mononitrates used were ethylene, propylene, and butylene glycol mononitrates, abbreviated as EGN, PGN, and BGN respectively. For their acrylates and methacrylates, the following abridged notations are used: ENA and ENMA, PNA and PNMA, and BNA and BNMA respectively. The monomer reactivity ratios, r_1 and r_2, and the Alfrey-Price Q_2 and e_2 values for ANA and ANMA were evaluated as follows: $r_1=0.48$, $r_2=0.08$, $Q_2=0.49$, and $e_2=1.00$ for ENA; $r_1=0.41$, $r_2=0.20$, $Q_2=0.69$, and $e_2=0.78$ for BNA; $r_1=0.35$, $r_2=0.49$, $Q_2=0.99$, and $e_2=0.53$ for ENMA; $r_1=0.36$, $r_2=0.50$, $Q_2=0.98$, and $e_2=0.51$ for PNMA and $r_1=0.37$, $r_2=0.40$, $Q_2=0.90$, and $e_2=0.58$ for BNMA. The polar and steric effects of the ester side chain containing the nitrate group were discussed. ANA was copolymerized with some other divinyl monomers, and the resulting crosslinked copolymer were subjected to the swelling test.

In a previous paper,1) the preparation and the radical polymerization of alkylene glycol nitrate acrylates (ANA) and methacrylates (ANMA) have been reported, and the activation energy of the overall polymerization of each monomers has been evaluated. However, no articles on the copolymerization of ANA and ANMA with other reactive monomers have been known to us. This paper will be concerned with the copolymerization of ANA and ANMA with styrene and some other divinyl monomers.

Experimental

Materials. ANA and ANMA were prepared by the same method as has been described in the previous paper1) and were redistilled before use. The physical constants of the monomers are shown in Table 1.

The alkylene glycol mononitrates used are ethylene, propylene, and butylene glycol mononitrates, abbreviated as EGN, PGN, and BGN respectively. For their acrylates and methacrylates, the following abridged notations are used: ENA and ENMA, PNA and PNMA, and BNA and BNMA respectively. PGN and BGN are mixtures of primary and secondary alcohols. Since the isomer ratio of PGN was determined as 4 (primary) : 1 (secondary) by Pujo and Boileau,2) that of BGN may reasonably be assumed to be nearly 4 : 1, also. The styrene used as a reference in the copolymerization was purified by the usual method and was redistilled before use. 2-Methyl-2-nitro-1,3-propylene diacrylate was prepared according to the method recently reported by Strumza and Altschular.3) Triethylene glycol dimethacrylate was prepared according to the literature.4)

Table 1. Physical constants of monomers

Monomer	Bp (°C/mmHg)	n_D^{20}	d_4^{20}
ENA	74—76/4	1.4490	1.252
PNA	81—82/4.5	1.4420	—
BNA	72—75/2.5	1.4440	1.152
ENMA	70—72/2	1.4495	1.203
PNMA	72—74/3	1.4443	1.150
BNMA	76—78/3	1.4458	1.126

Diallyl phthalate and diallyl maleate of the G.R. grade were used after purification by the usual method. 2,2′-Azobisisobutyronitrile (AIBN) of the G.R. grade was used after two recrystallizations from ethanol. Benzoyl peroxide (BPO) of the G.R. grade was used after two reprecipitations from chloroform-methanol. The acetone, methanol, and other solvents used were purified by the usual technique.

Copolymerization Procedure. The copolymerization of ANA and ANMA with styrene was carried out in a sealed glass tube in the presence of 6.1×10^{-3} mol/*l* of AIBN at 60°C. The resulting copolymers were precipitated by adding a large amount of methanol and were then reprecipitated from acetone-methanol. Most runs were stopped before the copolymerization proceeded to 5% conversion. The composition of the copolymers was determined by nitrogen analysis. The

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1) M. Moriya and T. Yamashita, *Kobunshi Kagaku*, in press.

2) A. M. Pujo and J. Boileau, *Mem. Poudres*, **37**, 35 (1955).

3) J. Strumza and S. Altschular, *Israel J. Chem.*, **1**, 106 (1963).

4) A. Ya. Drinberg, *Zh. Prinkl. Khim.*, **27**, 613 (1954).

monomer reactivity ratios, r_1 and r_2, were calculated by the method of Fineman and Ross.[5]

Copolymerization of ANA with Divinyl Monomers. The copolymerization of ANA with divinyl monomers (0.5—10.0 wt% on ANA) was conducted using 0.5 wt% BPO (on total monomers) in a sealed glass tube at 65°C for 40 hr. The equilibrium of the swelling was measured with disks of the resulting copolymers, 10 mm in diameter and 1 mm thick, placed in acetone at 20°C for 48 hr. The swelling ratio at equilibrium, Q_m, is given as follows:

$$Q_m = [W/0.7995 + W_0(1/\rho + 1/0.7995)]/(W_0/\rho)$$

where ρ is the density of the polymer, W_0 the weight of the polymer, W the weight of the copolymer after swelling, and 0.7995, the density of acetone at 20°C.

Results and Discussion

Copolymerization of ANA and ANMA with Styrene. The resulting copolymers were fluffy white masses. The decomposition temperature of the copolymers was determined to be 205—210°C by differential thermal analysis.

The results of the copolymerization of ANA and ANMA with styrene are summarized in Table 2. As the figures in Table 2 indicate, the rate of copolymerization increases with the concentration of ANA and ANMA in the monomer mixture.

The monomer reactivity ratios, r_1 and r_2, and the Alfrey-Price Q_2 and e_2 values of ANA and ANMA, together with the known values for unsubstituted alkyl acrylates and methacrylates, are shown in Table 3. The monomer-copolymer composition curves for ANA and ANMA, based on the data in Table 2, are shown in Figs. 1 and 2 respectively. From the figures (r_1r_2) in Table 3 and the curves in Figs. 1 and 2, it can be seen that the copolymers

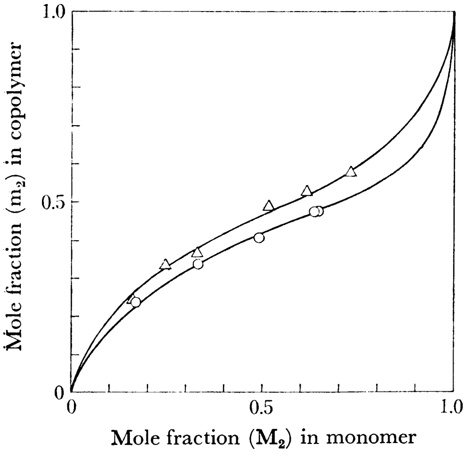

Fig. 1. Monomer-copolymer composition curves for the copolymerization of ANA with styrene.
○ (ENA), △ (BNA): found, ——: calculated

Table 2. The results of copolymerization of ANA and ANMA (M_2) with styrene (M_1) at 60°C

	[M_2] in comonomer mol fraction	Time (min)	Conversion (%)	N (%) in copolymer	[m_2] in copolymer mole fraction
ANA monomer					
ENA	0.169	300	2.5	2.79	0.234
	0.332	240	9.4	3.82	0.336
	0.491	260	5.0	4.47	0.406
	0.637	960	12.9	5.04	0.472
	0.645	1050	0.7	5.05	0.473
BNA	0.161	140	3.8	2.70	0.240
	0.247	125	3.5	3.45	0.333
	0.329	110	2.5	3.80	0.366
	0.518	55	1.5	4.68	0.484
	0.615	40	4.5	4.94	0.524
	0.730	40	7.1	5.26	0.573
ANMA monomer					
ENMA	0.098	70	0.7	2.32	0.195
	0.170	70	1.0	3.17	0.280
	0.357	70	1.4	4.60	0.445
	0.758	20	0.6	6.36	0.696
PNMA	0.123	135	2.0	2.56	0.225
	0.273	135	2.6	3.90	0.379
	0.414	70	1.9	4.63	0.478
	0.574	60	2.4	5.41	0.598
	0.652	55	3.3	5.66	0.640
	0.768	50	5.8	6.06	0.711
BNMA	0.147	90	1.9	2.79	0.258
	0.257	90	2.4	3.59	0.357
	0.384	85	3.3	4.12	0.431
	0.564	85	5.7	4.67	0.517
	0.615	60	4.8	4.99	0.572
	0.730	60	6.7	5.37	0.642

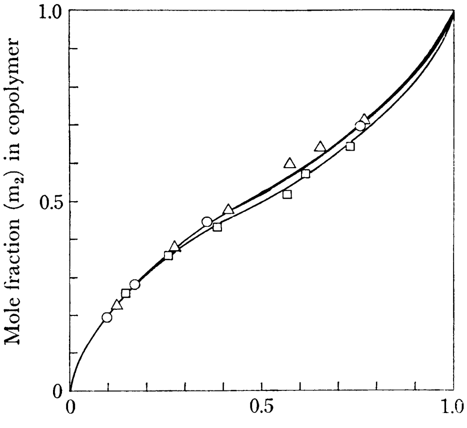

Fig. 2. Monomer-copolymer composition curves for the copolymerization of ANMA with styrene.
○ (ENMA), △ (PNMA), □ (BNMA): found
——: calculated

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[5] M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).

Table 3. Monomer reactivity ratios and Q_2 and e_2 values of ANA and ANMA at 60°C and these values of unsubstituted alkyl acrylates and methacrylates as references

M_2	r_1	r_2	$1/r_1$	r_1r_2	Q_2	e_2
ANA and ANMA						
ENA	0.48	0.08	2.08	0.038	0.49	1.00
BNA	0.41	0.20	2.44	0.082	0.69	0.78
ENMA	0.35	0.49	2.87	0.172	0.99	0.53
PNMA	0.36	0.50	2.78	0.180	0.98	0.51
BNMA	0.37	0.40	2.70	0.148	0.90	0.58
Unsubstituted alkyl acrylates and methacrylates						
MA (1)	0.75	0.18	1.34		0.42	0.60
EA (2)	0.77	0.17	1.30		0.42	0.62
n-BA (3)	0.82	0.21	1.22		0.43	0.53
IPA (4)	0.76	0.26	1.32		0.48	0.45
MMA (5)	0.52±0.02	0.46±0.02	1.92		0.74	0.40
EMA (6)	0.53±0.03	0.41±0.03	1.89		0.70	0.44
n-PMA (7)	0.57±0.01	0.38±0.04	1.76		0.65	0.44
IBMA (8)	0.55±0.02	0.40±0.05	1.82		0.68	0.43
n-BMA (9)	0.56±0.03	0.40±0.03	1.79		0.67	0.43

(1) CH_3; (2) C_2H_5; (3) n-C_4H_9; (4) i-C_3H_7 acrylates
(5) CH_3; (6) C_2H_5; (7) n-C_3H_7; (8) i-C_4H_9; (9) n-C_4H_9 methacrylates
(1) from Ref. 6, (2) and (4) from Ref. 8, (3) from Ref. 7, (5)—(9) from Ref. 9.

of ANA show a greater alternating tendency than a those of ANMA.

From Table 3, it may be seen that the relative reactivities, $1/r_1$, of ANA and ANMA to the attack of the polystyryl radical are larger than those of unsubstituted alkyl acrylates and methacrylates. Otsu *et al.*[8,9] have recently reported that the relative reactivities of alkyl acrylates and methacrylates to a polystyryl radical are correlated only with the polar substituent constant, σ^*, of the alkyl group in acrylates and methacrylates, and not with their steric substituent constant, E_s, in Taft's equation. The larger relative reactivities of ANA and ANMA in our experiments may also be ascribed to a strong polar effect of the alkyl group containing the nitrate group.

Taking it into consideration that the Q_2 and e_2 values for alkyl acrylates and methacrylates increase as a function of the electron-attracting nature of alkyl substituents,[8,9] the fact that these values for ANA and ANMA are larger than those of unsubstituted alkyl acrylates and methacrylates is readily explicable because of the strong electron-attracting nature of the nitrate group (see Table 4).

Table 4. Infrared spectroscopic data of acrylate and methacrylate monomers

	σ^* of alkyl group	$\nu_{C=O}$	ν_{C-O}	$1/r_1$	Q_2	e_2
Acrylate monomer						
EA (1)	−0.100	1726	1197	1.30	0.42	0.62
CLEA (2)	0.385	1727	1185	2.33	0.58	0.93
CNEA (3)	0.46	1728	1186	2.50	0.63	0.92
ENA		1728	1186	2.08	0.49	1.00
BNA		1726	1185	2.44	0.69	0.78
Methacrylate monomer						
EMA (4)	−0.100	1708	1177	1.89	0.68	0.43
BzMA (5)	0.215	1710	1165	2.27	0.86	0.42
CLEMA (6)	0.385	1717	1165	3.03	1.01	0.57
PhMA (7)	0.600	1730	1136	3.33	1.17	0.51
ENMA		1724	1165	2.87	0.99	0.53
PNMA		1715	1163	2.78	0.98	0.51
BNMA		1721	1166	2.70	0.90	0.58

(1) C_2H_5; (2) $CLCH_2CH_2$; (3) $CNCH_2CH_2$; (4) C_2H_5; (5) $C_6H_5CH_2$; (6) $CLCH_2CH_2$; (7) C_6H_5
(1)—(3) from Ref. 8, (4)—(7) from Ref. 9.
Determined with a Hitachi EPI-2 infrared spectrophotometer. Acrylate monomers were measured in liquid film and methacrylate monomers in solution of $C_2H_4Cl_2$.

The data of the infrared spectra for ANA and ANMA in Table 4 are consistent with the increased Q_2 values for these monomers, as Otsu *et al.*[8,9] have reported that the carbonyl-stretching frequencies in acrylates and methacrylates are shifted to a

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6) L. J. Young, *J. Polym. Sci.*, **54**, 411(1961).

7) "Encyclopedia of Polymer Science and Technology," Vol. 1, Interscience, New York (1964), p. 246.

8) T. Otsu, T. Ito, T. Fukumizu and M. Imoto, This Bulletin, **39**, 2257 (1966).

9) T. Otsu, T. Ito and M. Imoto, *Kogyo Kagaku Zasshi*, **69**, 986 (1966).

higher wave number as the electron-attracting character of alkyl substituents increases.

As compared with both ANA and ANMA, the $1/r_1$ and Q_2 values of ANA are smaller than those of ANMA, while the e_2 values of ANA are larger. This feature can presumably be attributed to the effect of the hyperconjugation and to the electron-releasing nature caused by the presence of the α-methyl group in ANMA.

Thus, the $1/r_1$, Q_2, and e_2 values of ANA and ANMA are larger than those of unsubstituted alkyl acrylates and methacrylates because of the polar effect of the alkyl group containing the nitrate group.

Copolymerization of ANA with Divinyl Monomers. The homopolymers of ANA reported in the previous paper are too soft and tacky to be utilized as elastomers in solid rocket propellants.[1] According to Matsuda *et al.*,[10] useful elastomers with good toughness properties have been produced by the copolymerization of nitrobutyl acrylate (nitro-BA) with some polyglycol dimethacrylates. Therefore, crosslinked polymers obtained by copolymerization with a small amount of divinyl monomers have been studied in this paper. The divinyl monomers used were diallyl phthalate (DAP), diallyl maleate (DAM), triethylene glycol dimethacrylate (TEDM), and 2-methyl-2-nitro-1,3-propylene diacrylate (MNPDA). The molecular weights of chains between crosslinking along main chains, M_c, were evaluated by the same calculation method as was used by Tanaka *et al.*[11] for the copolymers of nitro-BA with some divinyl monomers.

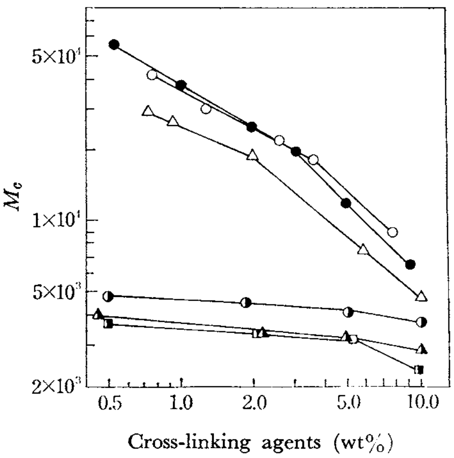

Fig. 3. Plot of M_c *vs.* divinyl monomer content
●: nitro-BA-TEDM, ○: BNA-TEDM,
△: BNA-MNPDA, ◑: BNA-DAP,
▲: BNA-DAM, ◨: ENA-DAM, ●: from Ref. 11

The relationship between the M_c value of the copolymers and the content of divinyl monomers in the monomer mixtures is plotted in Fig. 3, in which also some date for nitro-BA copolymers are given for the sake of comparison. It is found that the M_c value decreases with an increase in the content of crosslinking agents in the monomer mixtures. The M_c values of copolymers of BNA with TEDM are in the same order as those of the corresponding copolymers of nitro-BA. It may be noted that the copolymerization behavior of BNA with TEDM is similar to that of nitro-BA with TEDM.

Generally speaking, the M_c values are highest for TEDM copolymers, medium for MNPDA copolymers, and lowest for diallyl ester copolymers. As Tanaka *et al.*[11] have reported, with regard to nitro-BA copolymers, that the tensile strength and the hardness of the copolymers increase and the elongation values decrease with an increase in the crosslinking densities, the elongation values of the copolymers of BNA with diallyl esters appear to decrease with an increase in the crosslinking densities.

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[10] Y. Matsuda, A. Tanaka, K. Sasaki, R. Kawai, K. Matsumoto, N. Yoshida and Y. Matsui, Papers presented at the 2nd International Symposium on Rockets and Astronautics, Tokyo, Japan (1960), p. 1.

[11] A. Tanaka, K. Sasaki, Y. Hozumi and O. Hashimoto, *J. Appl. Polym. Sci.*, **8**, 1787 (1964).