

The Polymerization and Copolymerization of Nitroalkyl Acrylates and Nitroalkyl Methacrylates

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Synopsis

Nitroalkyl acrylates and methacrylates involving some new compounds were prepared. The homopolymerization of these monomers in toluene and their copolymerization with styrene in acetone were carried out with azobisisobutyronitrile as initiator. The rate of polymerization of the nitroalkyl acrylates showed a correlation with the number of nitro groups situated on the ester side chain. The apparent activation energies of the polymerization were found to be 22.0-27.5 kcal./mole for the nitroalkyl acrylates and about 11.5-13.0 kcal./mole for the nitroalkyl methacrylates. From the reactivity ratios and $Q-e$ values of the copolymerization the following information was obtained. The copolymerization behavior of nitroalkyl acrylates and methacrylates showed an alternating tendency, and these monomers belong to the conjugative monomer groups. On the reactivities of these monomers, the polarity of vinyl group was affected a little by nitro group of ester bond side, and the resonance affected little. These monomers were crosslinked with 2-methyl-2-nitro-1,3-propylene diacrylate. Some of the polymers showed marked improvement in the physical properties of elastomers.

INTRODUCTION

Nitroalkyl acrylates and methacrylates are interesting material in the field of solid rocket propellants. The radical polymerization and copolymerization of trinitroethyl methacrylate¹ and 2-nitrobutyl acrylate² have been reported.

The polymerization and copolymerization of these monomers are interesting to us, who have been investigating the utilization of nitro compounds as fuel binders of solid rocket propellants. In the work reported in this paper, nitroalkyl acrylates and methacrylates were prepared and their rate of homopolymerization and reactivity of copolymerization with styrene, with azobisisobutyronitrile (AIBN) as initiator, were investigated in an effort to determine the effects of nitro groups on the reactivity of the vinyl group. The physical properties of the fuel binders made from these monomers were then measured.

EXPERIMENTAL

Materials

Preparation of Nitroalcohols. 2-Nitro-1-propanol,³ 2-nitro-1-butanol,³ 3-nitro-1-butanol,³ 2-methyl-2-nitropropanol,³ and 2,2-dinitro-2-propanol⁴ were prepared according to the literature.

Preparation of Acrylic and Methacrylic Chloride. Acrylic chloride was prepared by the Moureu method,⁵ by the Stempel method,⁶ and in the reaction of acrylic acid with thionyl chloride. The methods of synthesis of methacrylic chloride reported by Khromov-Berisov and Yanovitskaya⁷ and Patai et al.⁸ were employed.

Preparation of Nitroalkyl Acrylates and Methacrylates. In a typical preparation 2-nitropropyl acrylate was prepared as follows. 2-Nitro-1-propanol, 21.0 g. (0.2 mole), acrylic chloride, 19.5 g. (0.22 mole), and carbon tetrachloride, 70 ml., were mixed in a 300 ml. flask equipped with a stirrer, condenser, and thermometer and then kept at 55–60°C. for 20 hr. After the reaction was completed, the unreacting chloride and solvent were distilled under reduced pressure, and the residue was washed several times with 50 ml. of water and dried with 50 g. of anhydrous sodium sulfate. Then 3 g. of silver powder was added to the product, and the mixture was distilled through a column 30 cm. long *in vacuo*. 2-Nitropropyl acrylate was distilled at 84°C. at 0.9 mm. Hg (lit.,⁹ 92°C. at 4 mm. Hg). For other monomers the preparation was carried out under various conditions; the results, with good yield, are shown in Table I.

Preparation of 2-Methyl-2-nitro-1,3-propylene Diacrylate. This compound was prepared according to the literature.¹⁰

Other Materials. Styrene was purified by an ordinal method. AIBN was used after recrystallization from ethanol. Toluene was dried over sodium hydroxide and distilled. Acetone was used after oxidation with potassium permanganate and distillation. Methanol was distilled after being boiled with calcium oxide.

Homopolymerization

Homopolymerization was carried out in toluene with AIBN as initiator. The rate of polymerization was measured dilatometrically. In a dilatometer of 30 ml. capacity a mixture of 0.02 mole of the monomer, 1 mole-% (based on the monomer) of AIBN, and 20 ml. of toluene was placed. After the content was degassed several times, dry nitrogen was introduced up to 450–500 mm. Hg. The reaction temperatures were controlled to ± 0.01 °C.

The densities of the polymers and monomers were measured with a pycnometer.

Copolymerization

Copolymerization was carried out in a sealed tube of 20 ml. capacity. Both monomers, AIBN, and acetone were placed in the tube. After de-

TABLE I
Reaction of Corresponding Acid Chloride with Nitroalcohols

Nitroalcohols, g.	Acid chloride, g.	Solvent, ml.	Temp., °C.	Time, hr.	B. p., (°C., mm. Hg.)	Yield	
						g.	%
2-Nitro-1-propanol, 16.4	AC, ^a 15.0	Benz., 60	65	20	50, 0.01	15	60
2-Nitro-1-butanol, 23.8	" , 18.1	CCl ₄ , 70	55	21	68, 0.01	22	60
2-Methyl-2-nitro propanol, 17.3	" , 13.6	" , 60	55	30	76, 0.9	13	50
3-Nitro-2-butanol, 23.8	" , 18.1	" , 60	55	21	54, 0.08	21.8	60
2,2-Dinitro pro- panol, 15.0	" , 10.5	" , 80	55	12	74, 0.07	13.0	55
2-Nitro-1-propanol, 21.8	MC, ^b 26.1	" , 50	60	18	62, 0.02	21.4	58
2-Nitro-1-butanol, 23.8	" , 26.1	Benz., 50	60	8	68, 0.42	24.0	65
3-Nitro-2-butanol, 23.8	" , 26.1	" , 60	60	22	85, 0.4	22.5	60
2-Methyl-2-nitro- 1-propanol, 23.8	" , 26.1	CCl ₄ , 60	60	23	69, 0.05	20.0	54
2,2-Dinitro propanol, 30.0	" , 26.1	Benz., 60	70	20	71, 0.04	19.5	47

^a AC, acrylic chloride.

^b MC, methacrylic chloride.

gassing the tube was sealed off. The reaction temperature was controlled to less than $\pm 0.01^\circ\text{C}$. Conversion was controlled to less than 10%. The content of the tube was poured into a large amount of methanol, to precipitate the product, and the precipitate was washed thoroughly, filtered, dried *in vacuo* at 80°C ., and weighed. The composition of the copolymer was determined by elementary analyses for N.

Elastomer Preparation

Monomer, 2-methyl-2-nitropropylene diacrylate (B), and AIBN were mixed, and the mixture was degassed and then poured into a glass cell.¹¹ The glass cell was kept for 3 days at 50°C . in an oven.

The tensile properties of the elastomers were determined on the basis of the Japanese Industrial Standard (Jis-K-6301): No. 3 test specimens were cut from an elastomer sheet with the standard "dogbone" tensile die.

A Shimazu autograph tensile tester (Model IS-500) was used to measure the tensile properties of the elastomers; an extension rate (initial) of 50 mm./min. was used for tensile strength and elongation measurements.

RESULTS AND DISCUSSION

Preparation of Nitroalkyl Acrylates and Methacrylates

A series of nitroalkyl acrylates and methacrylates was prepared from acrylic or methacrylic chloride and the corresponding nitroalcohols.

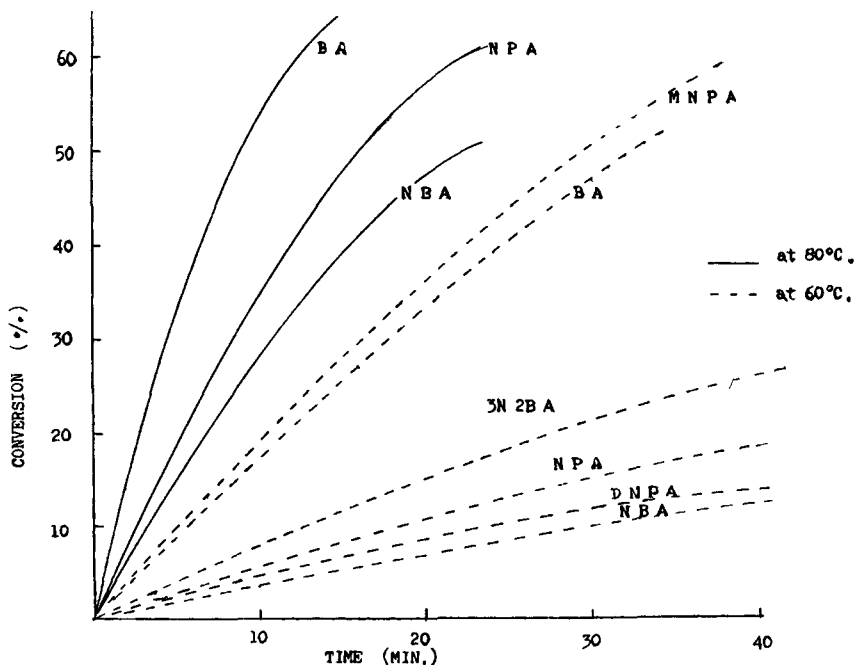


Fig. 1. Polymerization of nitroalkyl acrylates and butyl acrylate in toluene at (---) 60°C . and (—) 80°C .

TABLE II
Physical Constants of Monomers

Nitroalkyl acrylates and methacrylates	B.p., °C. and mm. Hg, and ref.	Elem. analysis N, %		n_D^{25} and ref.	Dens. at 60°C. and ref. at 25°C.
		Found	Calcd.		
2-Nitro-1-propylacrylate (NPA)	66, 0.4; 92, 4	8.47	8.47	1.4453, 1.4448	1.151, 1.143
2-Nitro-1-butylacrylate (NBA)	83, 0.8; 102, 6	7.80	8.09	1.4451, 1.4452	1.104, 1.112
3-Nitro-2-butylacrylate (3N2BA)	54, 0.08; —	7.88	8.09	1.4420, —	1.126, —
2-Methyl-2-nitropropylacrylate (MNPA)	80, 0.9; 102, 8	7.97	8.09	1.4450, 1.4455	1.104, 1.112
2,2-Dinitropropylacrylate (DNPA)	96, 0.2; 83, 1	13.47	13.73	1.4592, 1.4600	1.301, 1.303
2-Nitro-1-propylmethacrylate (NPMA)	62, 0.07; 109, 6	7.88	8.09	1.4475, 1.4470	1.105, 1.108
2-Nitro-1-butylmethacrylate (NBMA)	69, 0.4; 112, 8	7.16	7.49	1.4474, 1.4469	1.076, 1.085
2-Methyl-2-nitropropylacrylate (MNPHA)	69, 0.05; 102, 4	7.11	7.49	1.4479, 1.4471	1.082, 1.087
3-Nitro-2-butylmethacrylate (3N2BMA)	85, 0.04; —	7.10	7.49	1.4458, —	1.081, —
2,2-Dinitropropylmethacrylate (DNPMA)	83, 0.04; —	12.87	12.84	1.4600, —	—, —

Since some monomers have been prepared in the alcoholysis⁹ of methyl acrylate or methacrylate with nitroalcohol, we tried to repeat this process; we found that the first of these reactions was superior to the second in yield and purity of product. Using the ordinal method of reaction of acrylic or methacrylic chloride with nitroalcohol, we prepared each five nitroalkyl acrylates and methacrylates as shown in Table II.

Homopolymerization in Toluene with AIBN as Initiator

Time-conversion plots in the homopolymerization of nitroalkyl acrylates and methacrylates are shown in Figures 1 and 2. The monomer concentration in each case was fixed at 2.0 moles/l. The rate of nitroalkyl acrylates showed a correlation with the number of nitro groups separated from

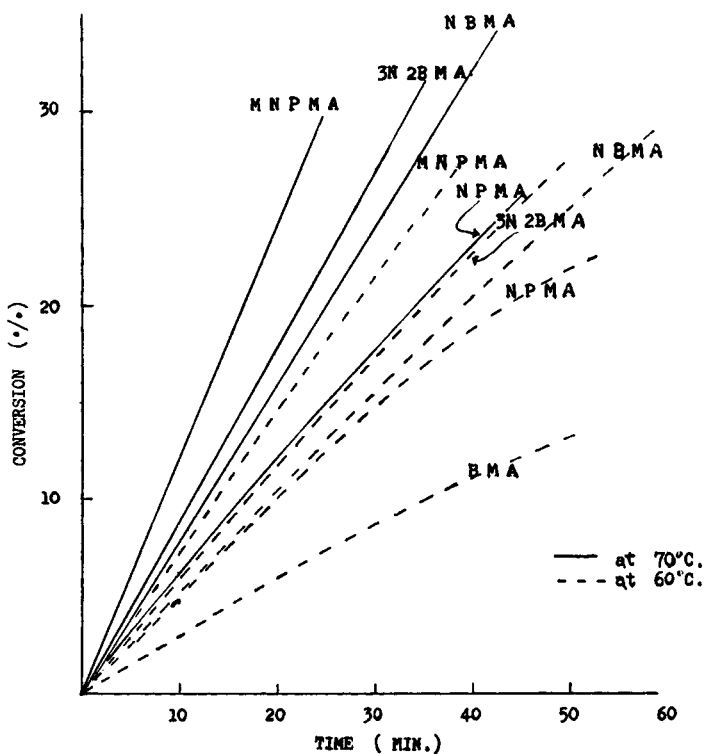


Fig. 2. Polymerization of nitroalkyl methacrylates and butyl methacrylate in toluene at (---) 60°C. and (—) 80°C.

the double bond by the ester group, but the rate of nitroalkylates did not. The behavior of the latter is not clear.

From an Arrhenius plot the apparent activation energies were calculated as shown in Table III. The values of the acrylates were as expected, but those of the methacrylates were rather lower than expected.

TABLE III
Activation Energies of Polymerization of Nitroalkyl Acrylates and Methacrylates^a

	<i>E</i> , kcal./mole
BA	22.0
NBA	27.5
NPA	23.1
BMA	12.0
NPMA	12.1
MNPMA	12.5
NBMA	11.4

^a For meanings of abbreviations see Table II.

Copolymerization Behavior of Nitroalkyl Acrylates and Methacrylates with Styrene

The copolymerization of the styrene-MNPMA system was typical for styrene-monomer systems. The results obtained are shown in Table IV.

The monomer reactivity ratios r_1 and r_2 were calculated for these systems according to the Fineman-Ross¹² and Mayo-Lewis¹³ method; (Figs. 3-6). From the r_1 and r_2 values the Q and e values proposed by Alfrey and Price¹⁴ were calculated for all the monomers by assuming the values for styrene to be $Q = 1.0$ and $e = -0.80$.

The results r_1 , r_2 , r_1r_2 , Q , and e are summarized in Table V and compared with those known for alkyl acrylates and methacrylates. Since the r_1 and r_2 of the nitroalkyl methacrylates, which are smaller than unity,

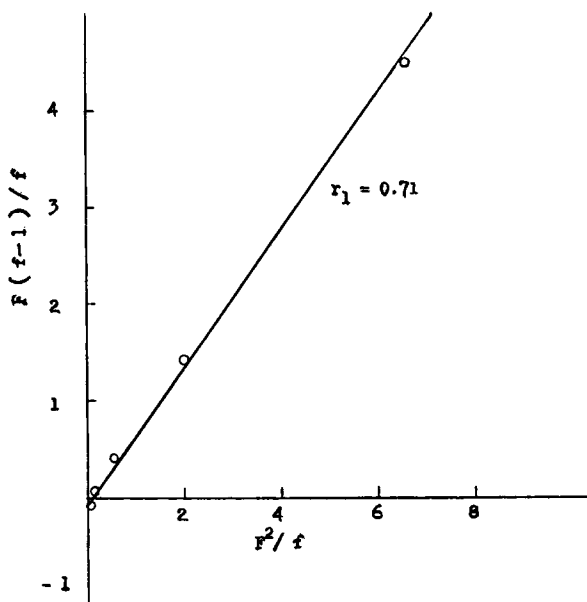


Fig. 3. Fineman-Ross plot of St-MNPA system.

TABLE IV
Results of Copolymerization of St-MNPMA System in Acetone
at $80 \pm 0.01^\circ\text{C}$.; AIBN = 0.1 mole-% Based on Monomer

Concn., moles (M_1, M_2)	Monom. compn., mole-% (M_1, M_2)	React. time, min.	Yield, wt.-%	Elem. anal. N, %	Copolym. comp., mole-% (M_1, M_2)
1.710, 0.310	84.7, 15.3	70	6.69	3.09	71.9, 28.1
1.390, 0.543	71.8, 28.2	60	7.11	3.99	61.1, 38.9
1.001, 0.995	50.2, 49.8	45	2.79	5.04	46.6, 53.4
0.667, 1.394	30.3, 69.7	30	4.13	5.60	37.6, 62.4
0.306, 1.658	15.6, 84.4	35	3.06	6.27	25.9, 74.1

TABLE V
Monomer Reactivity Ratios and Q and e Values for Nitroalkyl Acrylates and
Methacrylates at 80°C . and These Values for Alkyl Acrylates and
Methacrylates as References; $M_1 = \text{Styrene}$, $Q = 1.0$, $e = -0.8$

M_2	r_1	r_2	$r_1 r_2$	Temp., $^\circ\text{C}$.	Q	e
Nitroalkyl acrylates and methacrylates:						
NPMA	0.39	0.37	0.14		0.84	0.59
NBMA	0.25	0.34	0.085		1.14	0.77
3N2BMA	0.43	0.078	0.033		0.53	1.04
MNPMA	0.32	0.37	0.12		0.97	0.66
DNPMA	0.37	0.18	0.066		0.72	0.85
MNPA	0.71	0.08	0.057		0.40	0.76
3N2BA	0.58	0.13	0.075		0.47	0.81
Alkyl acrylates and methacrylates: ^a						
MMA ^b	0.50	0.50		60	0.74	0.40
EMA ^b	0.65	0.29		70	0.56	0.17
BMA ^b	0.64	0.54		70	0.72	-0.23
MA ^b	0.75	0.20		70	0.42	0.60
EA ^b	0.80	0.20		70	0.52	0.22
BA ^b	0.76	0.19		60	0.51	1.02
NBA ^c	0.58	0.115		70	0.47	0.85

^a MMA, methyl methacrylate; EMA, ethyl methacrylate; BMA, butyl methacrylate; MA, methyl acrylate; EA, ethyl acrylate; BA, butyl acrylate; NBA, 2-nitro-1-butylacrylate.

^b From Young.¹⁵

^c From Tanaka et al.²

and smaller than those of the alkyl methacrylates, their r_1r_2 are nearer to zero. Therefore, they show a greater alternating tendency. On the other hand, the r_1 and r_2 of the nitroalkyl acrylates are very close to those of the alkyl acrylates, so that the alternating tendencies seem to be similar.

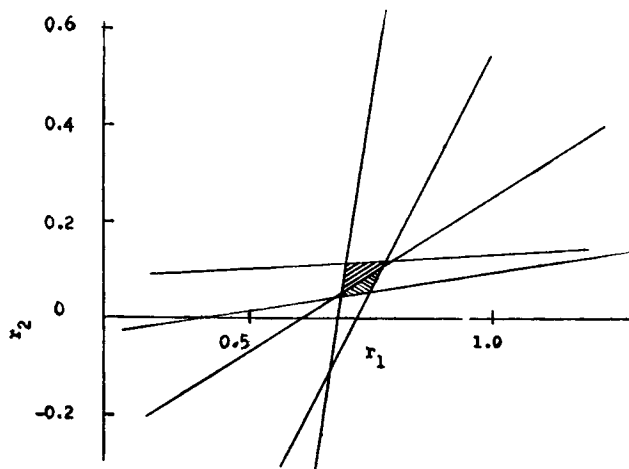


Fig. 4. Determination of r_2 of St-MNPA by Mayo-Lewis method.

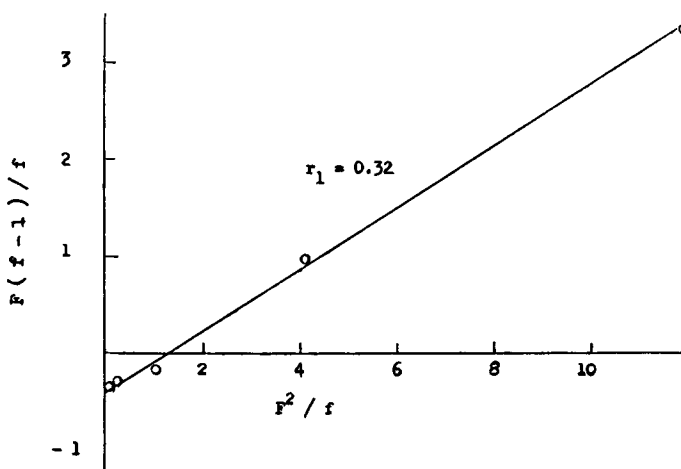


Fig. 5. Fineman-Ross plot of St-MNPMA system.

From a general point of view the Q values of the nitroalkyl acrylates and alkyl acrylates and of the nitroalkyl methacrylates and alkyl methacrylates were respectively similar. Those of the nitroalkyl acrylates and methacrylates are greater than the values of unconjugative monomers, such as vinyl chloride and vinyl acetate and therefore these monomers seem to belong to conjugative monomers.

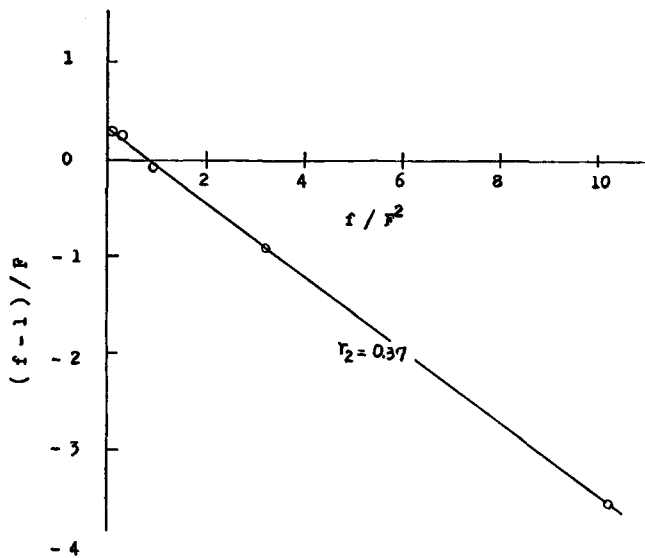


Fig. 6. Fineman-Ross plot of St-MNPMA system.

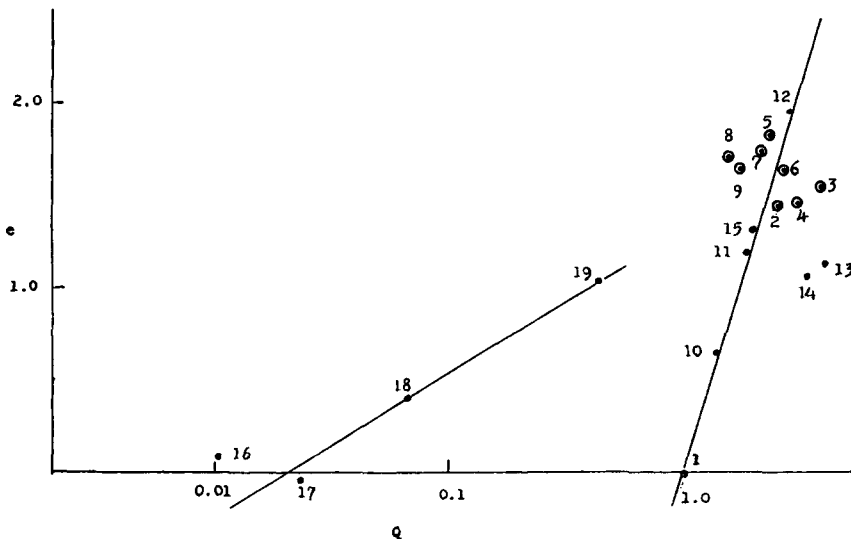


Fig. 7. Plot of Q versus e for nitroalkyl acrylates and methacrylates (for styrene $Q = 1.0$ and $e = 0$) (1) styrene, (2) NPMA, (3) NBMA, (4) MNPMA, (5) 3N2BMA, (6) DNPMA, (7) NPA, (8) MNPA, (9) 3N2BA, (10) *m*-chlorostyrene, (11) MMA, (12) acrylonitrile, (13) *p*-nitrostyrene, (14) *p*-cyanostyrene, (15) BA, (16) ethylene, (17) vinyl acetate, (18) vinyl chloride, (19) vinylidene chloride. Values 10-19 from ref. 16.

TABLE VI
Properties of Various Nitroalkyl Acrylate and Methacrylate Copolymers

	Compu., wt.-%		H/C ^b	Elong., %	Ult. tens. streng., kg./cm. ²	100% modul., kg./cm. ²	300% modul., kg./cm. ²	Dens. at 23°C., g./ml.
	B ^a	AIBN						
MNPA	94.2	3.9	1.41	480	0.4	0	0.1	1.205
NPA	94.7	3.0	1.50	690	1.2	0.1	0.3	1.276
3N2BA	93.7	4.1	1.41	580	0.9	0.1	0.6	1.238
DNPMA	95.6	2.6	1.33	50	4.2	—	—	1.379
BA	92.6	5.1	—	—	—	—	—	0.931
BMA	92.5	5.3	—	—	—	—	—	0.966

^a B, 2-methyl-2-nitro-1,3-propylene diacrylate.

^b Ratio hydrogen to carbon.

Here again, we attempted to summarize Q and e by using the Q - e scheme revised by Kawabata et al.,¹⁶ in which the values for styrene are 1.0 and 0, making for a better approximation; see Figure 7. Clearly, the plot is one of conjugative monomers.

Generally speaking, the e values of the nitroalkyl acrylates and methacrylates are a little greater than those of the alkyl acrylates and methacrylates, but the behavior of the former seems to be similar to that of the latter. It was concluded that in the former the nitro groups, which are separated from the double bond by an ester alkyl group, have little effect on the reactivity of the double bond.

Copolymerization of Nitroalkyl Acrylates and Methacrylates with 2-Methyl-2-nitro-1,3-propylene Diacrylate

From the fundamental data described above it was considered that the reactivity of the double bond in 2-methyl-2-nitro-1,3-propylene diacrylate is similar to that of 2-methyl-2-nitropropyl acrylate and that therefore the polymers obtained in the copolymerization of B and another conjugative monomer would show the alternating structure. Copolymerizations of nitroalkyl acrylates or methacrylates with B as crosslinking agent were carried out in an attempt to obtain useful elastomers for binders. The compositions and physical properties of the elastomer copolymers obtained are shown in Table VI. The crosslinked polymers (except for the polymer prepared from DNPMA) of Table VI showed elongations of 500–700% at break point but did not exhibit the tensile strength required for a binder in propellants.

This fault will be corrected by determining the amount of crosslinking required for optimal physical properties.

The densities of polymers containing the nitro group were greater than those of the polymers from alkyl acrylates and methacrylates. The density of a polymer depends upon the number of nitro groups. Greater density and hydrogen-to-carbon ratios of a binder are desirable ballistic properties of propellants.

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References

1. T. R. Fukuto and J. P. Kispersky, *Tetrahedron*, **19** (Suppl. 1), 105 (1963).
2. A. Tanaka, K. Sasaki, Y. Hozumi, and O. Hashimoto, *J. Appl. Polymer Sci.*, **8**, 1787 (1964).
3. B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).
4. H. E. Hamel, J. S. Dehn, J. A. Love, J. J. Scigliano, and A. H. Swift, *Ind. Eng. Chem. Prod. Res. Develop.*, **1**, 108 (1962).
5. C. Moureu, *Ann. Chim.*, **2**, 164 (1894); G. D. Jones, J. Zomlefer, and K. Hawkins, *J. Org. Chem.*, **9**, 500 (1944).
6. G. H. Stempel, Jr., R. T. Cross, and R. P. Mariella, *J. Am. Chem. Soc.*, **72**, 2299 (1950).

7. N. V. Khromov-Berisov and A. M. Yanovitskaya, *Zh. Obshch. Khim.*, **29**, 2663 (1959); *Chem. Abstr.*, **54**, 12143 (1960).
8. S. Patai, M. Bentov, and M. E. Reichman, *J. Am. Chem. Soc.*, **74**, 845 (1952).
9. N. S. Malans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 2125 (1950).
10. J. Strumza and S. Altschular, *Israel J. Chem.*, **1**, 106 (1963).
11. K. Yamazaki and H. Tokui, *Bull. Chem. Soc. Japan*, **39**, 1584 (1966).
12. M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).
13. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
14. T. Alfrey, Jr., and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).
15. L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).
16. N. Kawabata, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **51**, 70 (1962); *idem*, *J. Chem. Soc. Japan*, Ind. Chem. Sect., **65**, 60 (1962).

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