

Polymerizations of Nitroalkyl Acrylates

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Synopsis

We have prepared some nitroalkyl acrylates and methacrylates by a method involving alcoholysis, and investigated their polymerizability. 2-Nitrobutyl acrylate (NBA) was extensively studied. The especially purified NBA monomer has good polymerizability without inhibiting radical polymerization and gives a thermally stable polymer. From copolymerization experiments with styrene, methyl methacrylate, and acrylonitrile, the Q and e values of NBA were estimated to be 0.47 and 0.85, respectively. The copolymerization behavior of NBA with some polyglycol dimethacrylates and unsaturated polyesters are comparable to those of *n*-butyl acrylate. This monomer has little tendency to polymerize with organometallic initiators, but some polymers obtained are found to be crystalline. The polar and steric effects of the nitro group situated on the ester side chain are discussed.

Recently it has become important to utilize nitro compounds in the field of solid rocket propellants.¹ With the aim of producing propellants of high performance, we have investigated new fuel binders having oxidizable oxygen in the molecules, such as polymers containing nitro or nitrate groups.

First of all, we studied the preparation of nitroalkyl acrylates and methacrylates, and their applications. Only several reports²⁻⁴ have been published on nitroalkyl acrylate.²

Thus, the object of this present study is to investigate polymerizations and copolymerizations of nitroalkyl acrylates in comparison with alkyl acrylate, and to discuss the effects of the nitro group on both polymerization behavior and structure of the polymers. Among them, 2-nitrobutyl acrylate has been extensively studied.

EXPERIMENTAL

Methods

The polymerizations and copolymerizations were carried out in sealed glass tubes by normal bulk polymerization procedures under nitrogen. Polymers were purified by reprecipitation from acetone solutions in methanol, followed by drying for 24 hr. at 50°C. under vacuum. The polymerizations with organometallic catalysts were performed by solution polymeriza-

tion methods, at -78°C . (in Dry Ice-methanol). After a definite time interval, the polymerization was stopped by adding methanol containing hydrochloric acid. The polymer thus formed was separated and purified in the usual way.

Viscosities of polymers in acetone were measured with an Ostwald viscometer at 30°C . Compositions of copolymers were determined by micro-Dumas method. The equilibrium of swelling was measured on disks of polymers 10 mm. in diameter and 1 mm. in thickness in acetone at 20°C . for 24 hr. The swelling ratio at equilibrium, q_m , is given as follows:

$$q_m = \left[\frac{W}{0.7995} + W_0 \left(\frac{1}{\rho} - \frac{1}{0.7995} \right) \right] / \left(\frac{W_0}{\rho} \right) \quad (1)$$

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

X-ray powder diffraction patterns were obtained with a recording Geiger counter ($\text{CuK}\alpha$).

Materials

Nitroalkyl Acrylates and Methacrylates. These monomers were prepared by alcoholysis reaction from methyl acrylate or methacrylate and the corresponding nitroalcohols (made by Commercial Solvents & Co.), according to the method of Marans and Zelinski.² Monomers prepared are summarized in Table I.

In a typical preparation, 2-nitrobutyl acrylate monomer was prepared as follows. 2-nitro-1-butanol (90 g.), methyl acrylate (260 g.), xylene (360 g.), *p*-toluene-sulfonic acid (15 g.), and copper powder (10 g.), were mixed in a 2000 cc. three-necked flask equipped with a stirrer, thermometer, and a distillation column, then heated from 70 to 110°C . and kept at this temperature until no more methanol was distilled off. After reaction was completed, the copper powder was filtered off, and the liquid product was washed several times with water and 1% aqueous NaOH solutions in a separatory funnel. Then, the product was distilled under vacuum. 2-Nitrobutyl acrylate distilled at 120 – $130^{\circ}\text{C}/5$ mm. Hg. Monomer thus purified is almost colorless.

The purity of the monomer was determined by the pyridine sulfate dibromide method.⁵

Other Vinyl Monomers. Styrene, acrylonitrile, methyl methacrylate, *n*-butyl acrylate, diallyl phthalate, and diallyl ether were used after purification of chemically pure grade reagents by the usual methods, and triethylene or polyethylene glycol dimethacrylate monomers were used as the commercially available products without distillation (MG-1 made by Union Carbide Chemicals, SR-205 and SR-210 made by Sartomer Resins Co.).

TABLE I
Preparation of Nitroalkyl Acrylate and Methacrylate Monomers and Polymers

Acrylate	Monomer			Polymer
	Starting material ^a	Yield, %	Purity, % ^b	
2-Nitroethyl acrylate	2-Nitro-1-ethanol	25.5	—	Pale yellow, transparent, rubberlike polymer; sol. in acetone; brittle at low temp. (−20°C.)
2-Nitropropyl acrylate	2-Nitro-1-propanol	64.2		Same as above
2-Nitrobutyl acrylate	2-Nitro-1-butanol	47.7	95.0	Pale yellow, transparent, tacky, soft rubberlike polymer; flexible at low temp. (−15°C.)
2-Nitro-2-methylpropyl acrylate	2-Nitro-2-methyl-1-propanol	37.1	96.1	Pale yellow, transparent, hard polymer
2-Nitropropyl methacrylate	2-Nitro-1-propanol	55.0	94.5	Pale yellow, transparent, hard polymer; brittle
2-Nitrobutyl methacrylate	2-Nitro-1-butanol	36.0	98.0	Pale yellow, transparent, hard polymer; brittle

^a Monomers were prepared by alcoholysis with methyl acrylate or methacrylate.

^b The purities of monomers were determined by the pyridine dibromide sulfate method.

Unsaturated Polyesters. Unsaturated polyesters were prepared from propylene glycol, maleic anhydride, and adipic acid by polyesterification reactions.

Initiators. Benzoyl peroxide (BPO), methyl ethyl ketone peroxide (MEKPO), and *tert*-butyl hydroperoxide (tBHPO) used were commercial materials of the highest quality, and their active oxygens were titrated before use.

Diethylzinc was obtained commercially. Grignard reagent, alkyl lithium, ketyl compound, and diethylaluminum diphenylamide were prepared according to standard methods.

RESULTS

Homopolymers of Nitroalkyl Acrylates and Methacrylates

Marans and Zelinski² reported on preparation of nitroalkyl acrylate and methacrylate monomers, and on examination of their polymerizability. Rehberg et al.³ reported on the glass transition temperatures of 2-nitro-2-methylpropyl acrylate in comparison with other acrylate polymers.

Marvel et al.⁴ prepared a copolymer of butadiene and 2-nitro-2-methylpropyl acrylate, and evaluated it as a synthetic rubber.

We have examined preparation of these monomers and polymers and especially studied the influence of the purity of monomers on the properties of the polymers. Results are shown in Tables I and II.

TABLE II
Effect of the Purity of Nitrobutyl Acrylate Monomers on Polymer Properties^a

Purity of NBA monomer, %	Polymer properties
79.6	Polymerized incompletely; fragile
85.5	Upper part is tacky
89.25	Same as above
96.4	Polymerized almost completely; tough
96.4 (0.3% 2-nitro-1-butylene added ^b)	Polymerized incompletely, fragile
96.4 (1.0% 2-nitro-1-butanol added)	Polymerized almost completely, tough

^a Polymerization conditions: 2-nitrobutyl acrylate monomer (NBA), 10 g.; polyethylene glycol dimethacrylate (MG-1), 0.2 g.; initiator, benzoyl peroxide 0.1% and *tert*-butyl hydroperoxide 0.1% (by weight on NBA monomer); temp. 70°C.; time 24 hr.

^b Nitrobutylene was prepared by dehydration of 2-nitro-1-butanol with phosphoric acid at 170–180°C.

In preparing monomers by the method of acid-catalyzed alcoholysis, some unreacted nitroalcohols are included in the monomers as impurities, and these alcohols are transformed into nitroolefins in heating; these latter seem to retard the polymerization of monomers and to weaken the physical properties of polymers formed. Therefore, purification of crude monomers must be carried out as completely as possible by washing with water and 1% aqueous alkaline solution and by distilling under vacuum. Also, we found that the performance and the thermal stability of composite rocket propellants produced with purified 2-nitrobutyl acrylate monomer are far superior to those prepared from unpurified monomer.

From the results of above tables it is concluded that the nitroalkyl acrylates must be at least 94–95% pure in practical use. The polymerizability of 2-nitrobutyl acrylate thus obtained and free from such impurities as nitroolefin and nitroalcohol was examined in more detail.

Polymerization Kinetics of 2-Nitrobutyl Acrylate

Polymerizations of 2-nitrobutyl acrylate (NBA) monomer of 94.8% purity were carried out at temperatures 60–80°C. with peroxide initiator, and the results compared with polymerization of *n*-butyl acrylate. Here, we have adopted a mixed peroxidic initiator of BPO-tBHPO in order to avoid deadend polymerization.

Polymerization recipes are shown in Table III.

TABLE III
Conditions of Polymerization of NBA

No.	tBHPO (on monomer)		BPO (on monomer)		Temp., °C.
	Wt.-%	Mole-%	Wt.-%	Mole-%	
3-1	0.1	0.192	0.1	0.071	60
3-2	0.3	0.575	0.3	0.214	60
3-3	0.5	0.958	0.5	0.356	60
3-4	0.7	1.339	0.7	0.498	60
3-5	0.3	0.575	0.3	0.214	70
3-6	0.3	0.575	0.3	0.214	80
B (<i>n</i> -butyl acrylate)	0.2	0.284	0.2 ^a		60

^a 5% monomer soln. of cobalt naphthenate added.

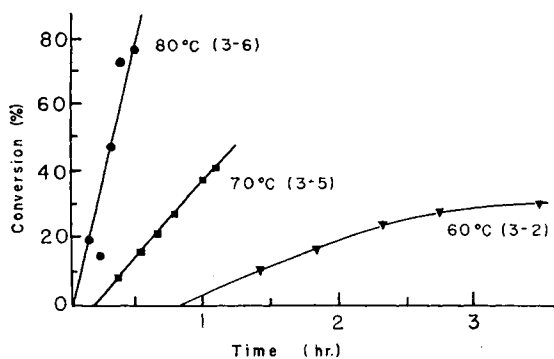


Fig. 1. Polymerizations of nitrobutyl acrylate at 60–80°C.

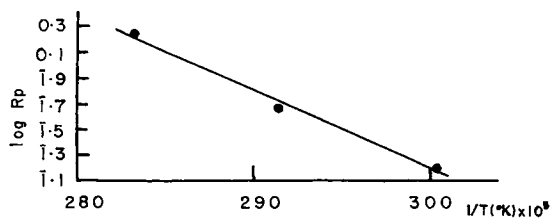


Fig. 2. Plot of $\log R_p$ vs. $1/T$.

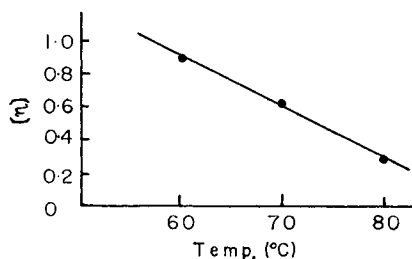


Fig. 3. Relationship between intrinsic viscosities of polymers initially formed and temperature of polymerization.

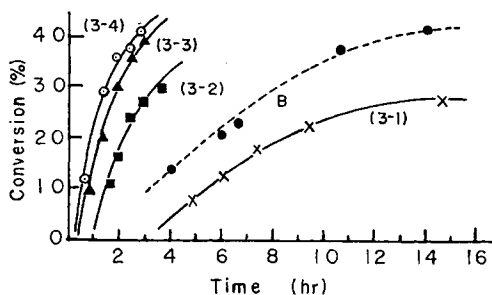


Fig. 4. Polymerization of nitrobutyl acrylate at 60°C. at various initiator concentrations.

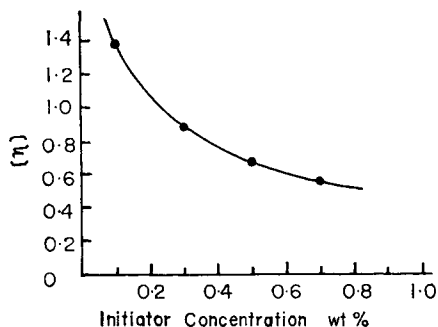


Fig. 5. Effect of initiator concentration on intrinsic viscosity of polymers formed.

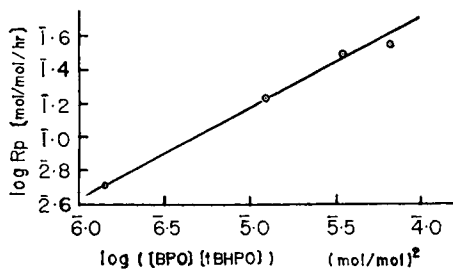


Fig. 6. Relationship between initial rates and initiator concentrations.

Time-conversion curves at constant catalyst concentration are illustrated in Figure 1. From an Arrhenius plot of initial polymerization rates and reciprocal absolute temperature (Fig. 2), the apparent activation energy of polymerization of NBA is calculated to be 28.6 kcal./mole. This value is rather higher than expected; however, we do not consider it abnormal, because this higher value may be ascribed in part to a higher E_t value of mixed peroxidic initiator used according to following equation:

$$E = E_p + \frac{1}{2} E_i - E_t \quad (2)$$

where E_p , E_i , and E_t are the activation energy of propagation, initiation, and termination, respectively.

The relationship between intrinsic viscosities of polymers initially formed and temperatures of polymerization is shown in Figure 3. Time-conversion curves with varying initiator concentrations at 60°C. are illustrated in Figure 4. In Figure 5 intrinsic viscosities of polymers are plotted against various initiator concentrations.

From a linear relationship on log-log plots between initiator concentrations and initial polymerization rates at 60°C. (Fig. 6) we are able to realize the square-root rule as follows:

$$R_p \propto [\text{BPO}]^{1/2} [\text{tBHPO}]^{1/2} \quad (3)$$

In conclusion, we can say that 2-nitrobutyl acrylate monomer undergoes a typical radical polymerization, comparable to *n*-butyl acrylate, in spite of containing a nitro group in the molecule.

Copolymerization of 2-Nitrobutyl Acrylate (NBA)

Copolymerizations of NBA with styrene, acrylonitrile, or methyl methacrylate were carried out in glass tubes. Results are shown in Figure 7. Monomer reactivity ratios obtained by the method of Fineman-Ross are tabulated in Table IV, and these results compared with those for other acrylates.⁶⁻⁸

From these results *Q* and *e* values in the Alfrey-Price equation are calculated as 0.47 and 0.85, respectively (Table V). It can be seen that the character of the NBA monomer is closer to *n*-butyl acrylate than methyl acrylate, and still closer to β -chloroethyl acrylate, as a result of the presence of an electron-attractive nitro group adjacent (in β -position) to the carboxyl group.

In other copolymerization experiments, for example, in curing of unsaturated polyesters with some vinyl monomers, NBA is observed to behave similar to *n*-butyl acrylate (Table VI). In other words, the behavior of NBA polymerization to a fumarate unit formed by isomerization from

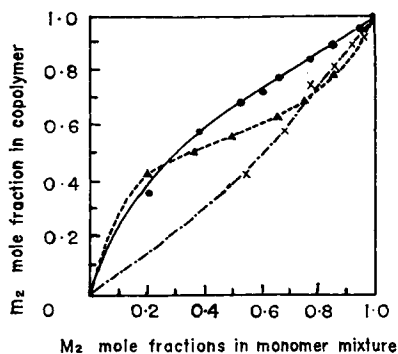


Fig. 7. Monomer-copolymer composition curves for 2-nitrobutyl acrylate with (▲) styrene; (●) methyl methacrylate; and (×) acrylonitrile. Bulk polymerization; BPO as initiator at 70°C.

TABLE IV
Monomer Reactivity Ratios in Copolymerizations of Some Acrylates

M ₁	M ₂	r ₁	r ₂	Temp., °C.	Reference
2-Nitrobutyl acrylate	Styrene	0.115	0.58	70	Present work
	Methyl methacrylate	0.22	1.60	70	
	Acrylonitrile	1.58	0.90	70	
Methyl acrylate	Styrene	0.18 ± 0.02	0.75 ± 0.07	60	Alfrey et al. ⁶
	Acrylonitrile	1.26 ± 0.1	0.67 ± 0.1	60	Alfrey et al. ⁶
<i>n</i> -Butyl acrylate	Styrene	0.16 ± 0.04	0.49 ± 0.04	60	Arlman and Melville ⁷
	Acrylonitrile	1.2 ± 0.1	0.89 ± 0.08	60	Tamikado and Iwakura ⁸

TABLE V
Q and *e* Values of Some Acrylates

Acrylate	<i>Q</i>	<i>e</i>	Reference
Methyl acrylate	0.42	0.60	Young ⁹
Ethyl acrylate	0.42	0.60	Unruh and Laakso ¹⁰
<i>n</i> -Butyl acrylate	0.57	0.80	Calculated from data of Arlman and Melville ⁷
β -Chloroethyl acrylate	0.46	0.90	Price ¹¹
2-Nitrobutyl acrylate	0.47	0.85	Present work
Methyl methacrylate	0.74	0.42	Young ⁹

maleate in polyesterification¹² is closer to that of butyl acrylate than styrene or methyl methacrylate.

Copolymerizations of NBA with Divinyl Monomers

The homopolymer of NBA is too soft and tacky to be utilized as an elastomer, and so we have studied crosslinked polymers obtained by copolymerization with small portions of divinyl monomers. The divinyl monomers used were various polyglycol dimethacrylates and diallyl compounds.

Copolymerizations of NBA with these monomers (0.5–10.0 wt.-% on NBA) were performed with the use of 0.3% BPO and 0.3% tBHPO (on total monomers) at 65°C. for 40 hr. Degrees of crosslinking in these copolymers were measured by swelling in acetone at 20°C. and calculated from Flory's equation,¹³ it being assumed that μ values of these polymers were the same as that of poly(ethyl acrylate) in acetone ($\mu = 0.45$). Crosslinking densities ρ_e and molecular weights between crosslinks along main chains M_c were calculated from eqs. (4) and (5), respectively.

$$\rho_e = 11.917 \times 10^{-2} / \rho q_m^{5/3} \quad (4)$$

TABLE VI
 Curing of Unsaturated Polyesters with Various Vinyl Monomers^a

No.	Unsaturated polyester mole ratio				Vinyl monomer ^b	Cured polymer	
	Pro-pylene glycol	Adipic acid	Maleic anhydride	Acid value		Appearance	Durometer hardness
7-1-1	1.0	0.9	0.1	117	St	Clear, glass-like, brittle	96
7-1-2					MMA	Clear, flexible	37
7-1-3					NBA	Not completely cured	—
7-1-4					BA	"	—
7-2-1	1.0	0.6	0.4	102	NBA	"	—
7-2-2					BA	Translucent, flexible	14
7-3-1	1.0	0.4	0.6	96.6	St	Clear, glasslike	96
7-3-2					MMA	Clear, flexible, tough	84
7-3-3					NBMA	"	60
7-3-4					NBA	Clear, elastomeric	50
7-3-5					BA	"	42

^a Unsaturated polyester: vinyl monomer = 60:40 (by weight); Curing Conditions: catalyst added MEKPO 2%, Conaphthenate 0.1% (on total reactants, by weight), 70°C., 25 hr.

^b St = styrene; MMA = methyl methacrylate; BA = *n*-butyl acrylate; NBMA = 2-nitrobutyl methacrylate.

where ρ is the density of the polymer and q_m is the swelling ratio given by eq. (1) and

$$M_c = M_0/\rho_e \quad (5)$$

where M_0 is the molecular weight of the monomer unit.

Relations between M_c of copolymers and contents of divinyl compounds in monomer mixtures are plotted in Figure 8; data for butyl acrylate copolymers are given for comparison. The M_c values of copolymers of NBA with dimethacrylate are in same order as those of corresponding copolymers of butyl acrylate. It can be pointed out that the copolymerization behavior of NBA is similar to that of *n*-butyl acrylate in these systems, too.

Generally speaking, crosslinking densities of dimethacrylate copolymers are highest, these of diallyl ester copolymers are less, and those of diallyl ether copolymers are the lowest. The tensile strength and hardness of the copolymers increase with increasing crosslinking densities, and the elongation values decrease. Useful elastomers having good toughness properties are produced in copolymerization of NBA with some polyglycol dimethacrylates.¹⁴

Copolymers with diallyl ether are not sufficiently tough; this fact may

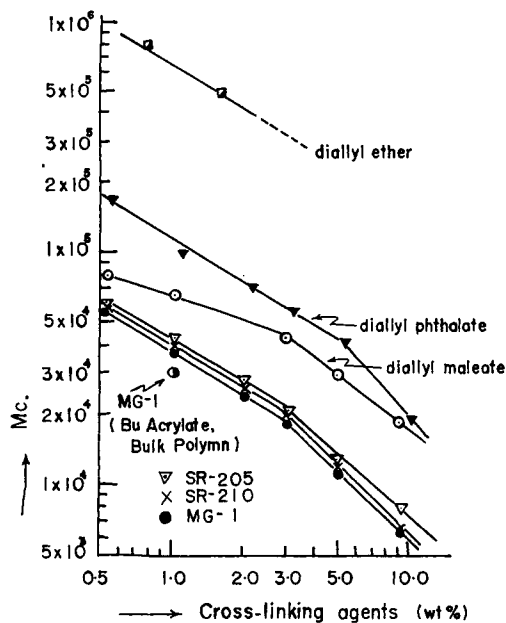


Fig. 8. Plot of M_c vs. divinyl monomer content.

be ascribed to a tendency for degradative chain transfer or cyclopolymerization of diallyl compounds.

The copolymerization of NBA with higher acrylates in the presence of small proportions of polyethyleneglycol dimethacrylate monomer can be carried out for the purpose of internal plasticization; these results are given elsewhere.

Polymerizations of NBA with the Use of Organometallic Initiators

Miller¹⁵ and Garrett¹⁶ reported on crystalline polymers of acrylates, especially *tert*-butyl, *sec*-butyl, and isobutyl esters. Furukawa et al.¹⁷ reported that *n*-butyl acrylate polymer prepared with organometallic initiator was amorphous by x-ray measurement, although poly(acrylic acid) prepared by saponification of this poly(butyl acrylate) was found to be stereoregular.

In order to investigate both effects of the nitro group, e.g., steric effect on the *n*-butyl substituent and polar effect on the double bond of the acrylate, we carried out polymerizations of NBA using various organometallic initiators. Results are shown in Table VII.

From these results it is concluded that NBA has little tendency for anionic polymerization, as is the case for *n*-alkyl acrylate. The polar effect of the nitro group on the double bond is small.

However, the polymers of NBA obtained from purified monomer with $Zn(C_2H_5)_2$ or $(C_2H_5)_2AlN(C_6H_5)_2$ are white powders and are found by x-ray measurements to be crystalline polymers after treatment with a solvent

TABLE VII
Polymerizations of NBA with Organometallic Initiators^a

Initiator	Solvent	Yield, %
Diethylzinc	<i>n</i> -Hexane	7.0
Ethylmagnesium bromide	<i>n</i> -Hexane	Trace
<i>n</i> -Butyllithium	<i>n</i> -Hexane	None
Disodium benzophenone	Tetrahydrofuran	None
Lithium dispersion (in wax)	Toluene	None
Diethylaluminum diphenyl amide	Toluene	8.0 (72 hr.)

^a Polymerization conditions: monomer, 10 g. (0.056 mole); solvent, 30 ml.; initiator, 0.0049 mole; temperature, -78°C .; time, 24 hr.

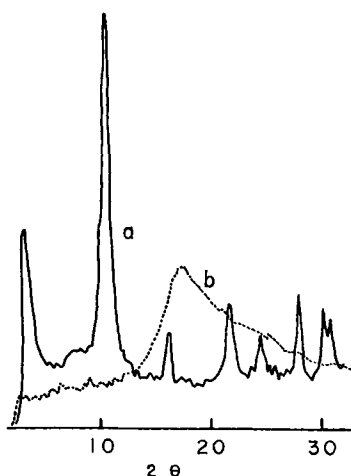


Fig. 9. X-ray diffraction patterns of poly(nitrobutyl acrylates); (a) polymer prepared with ZnEt_2 at -78°C .; (b) polymer prepared with tBHPO at 60°C .

(Fig. 9). The formation of crystalline polymer at low temperature may be due to the steric effect of the nitro group in the side chain. The crystal structures of these polymers are under investigation.

DISCUSSION

Nitroolefins polymerize easily in the presence of moisture and basic substances (anionic polymerization),^{18,19} and, generally, their polymers are known to be unstable under normal conditions. These characteristics of nitroolefins may be ascribed to the presence of the nitro group attached to the double bond.

We have studied nitroalkyl acrylates with especial attention to the effects of nitro group separated from the double bond by ester group. The effects of the nitro group considered are: (1) inhibiting action for radical polymerization, (2) polar effect on the double bond, (3) steric effect on the side chain (substituent), and (4) deterioration of thermal stability of polymer.

It is concluded that, especially in the case of 2-nitrobutyl acrylate, the purified monomer shows good polymerizability without inhibiting action for radical polymerization, and gives thermally stable polymers. On the basis of Q and e values of nitrobutyl acrylate ($Q = 0.47$, $e = 0.85$), it can be inferred that the polar effect of nitro-group separated from the double bond by an ester alkyl group is quite small, and this monomer has little tendency to polymerize with anionic initiators. The steric effect of nitro group in butyl substituent are realized in the formation of a crystalline polymer of nitrobutyl acrylate at low polymerization temperature.

Generally speaking, the behavior of 2-nitrobutyl acrylate seems to be similar to that of *n*-butyl acrylate. In order to ascertain quantitatively the polar effect of the nitro group positioned on an alkyl ester substituent, it will be necessary to investigate other nitroalkyl acrylates systematically.

Our qualitative investigation shows that 2-nitro-2-methylpropyl acrylate resembles 2-nitrobutyl acrylate in polymerization behavior.

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Résumé

On a préparé des acrylates et méthacrylates de nitroalcoyle par alcoolysse et on en a étudié la polymérisation. Parmi eux on a surtout étudié le 2-nitrobutyle acrylate (NBA). Le NBA fortement purifié polymérise bien, sans action inibitrice pour la polymérisation radicalaire, et donne un polymère qui est thermiquement stable. A partir des expériences

de copolymérisation avec le styrène, le méthacrylate de méthyle et l'acrylonitrile, on a estimé les valeurs de Q et e du NBA à 0,47 et 0,85. On peut comparer la polymérisation du NBA avec des diméthacrylates de polyglycol et des esters non-saturés avec la copolymérisation de l'acrylate de *n*-butyle. Ce monomère n'a qu'une faible tendance à polymériser avec des initiateurs organométalliques, mais certains polymères obtenus sont cristallins. On discute l'effet polaire et stérique des groupements nitrés, placés sur l'ester de la chaîne latérale.

Zusammenfassung

Einige Nitroalkylacrylate und -methacrylate wurden nach einer Alkoholysmethode hergestellt und hinsichtlich ihrer Polymerisationsfähigkeit untersucht. Besonders eingehend wurde 2-Nitrobutylacrylat (NBA) untersucht. Das besonders gereinigte NBA-Monomere ist gut polymerisierbar, zeigt keine Inhibitorwirkung bezüglich der radikalischen Polymerisation und ergibt ein thermisch stabiles Polymeres. Durch Copolymerisationsversuche mit Styrol, Methylmethacrylat und Acrylnitril wurden die Q - und e -Werte von NBA zu 0,47 bzw. 0,85 bestimmt. Das Copolymerisationsverhalten von NBA mit gewissen Polyglycoldimethacrylaten ist demjenigen von *n*-Butylacrylat ähnlich. Das Monomere zeigt nur geringe Tendenz zur Polymerisation mit organometallischen Startern, doch waren einige hergestellte Polymere kristallin. Die polaren und sterischen Effekte der an der Esterseitenkette befindlichen Nitrogruppe werden diskutiert.

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