

Methyl α -Cyanoacrylate. II. Copolymerization Studies*

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Synopsis

Copolymerization of methyl α -cyanoacrylate with five reference monomers gave values $e = +2.1$ and of $\log Q = 0.65$, with much scatter in the latter value. Alternating copolymers are formed by copolymerization with monomers of $e = -0.8$ or less. Bulk copolymerization with such monomers could not be accomplished, as a rapid noncatalyzed polymerization occurred upon mixing even at 0°C. Random copolymers with methyl methacrylate could be prepared in bulk; those with ca. 10% methyl methacrylate had physical properties similar to the homopolymer of methyl α -cyanoacrylate, except that the heat distortion temperature was lowered 10–15°C. The alternating copolymers were more thermally stable than the random copolymers. Glass temperature values for alternating copolymers do not appear to agree with values predicted from equations for random copolymers.

In the first paper of this series,¹ we discussed the free radical-initiated homopolymerization of methyl α -cyanoacrylate (MCyA) and compared its behavior with that of vinylidene cyanide. Gilbert and co-workers² have reported an extensive study of the free radical-initiated copolymerization of vinylidene cyanide with a variety of monomers and have determined the Q and e parameters. The present study was undertaken to compare the reactivity of MCyA in similar copolymerizations and also to determine some properties of the copolymers formed, as it was hoped that certain deficiencies in poly(methyl α -cyanoacrylate) could be corrected in this manner. Although difficulties were encountered in the quantitative determination of reactivity ratios, the qualitative observations on the preparation and properties of these copolymers should be of interest.

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POLYMERIZATION BEHAVIOR

Bulk Free Radical Copolymerization

Preparation of copolymers by bulk techniques was desired for direct comparison of properties with MCyA homopolymer. As discussed below, MCyA shows a strong tendency to form alternating copolymers with interesting properties when copolymerized in solution with monomers with negative e values. However, when equimolar quantities of MCyA and, e.g., α -methylstyrene were mixed in bulk at temperatures as low as 0°C., a rapid, exothermic polymerization occurred, even in the absence of any free radical initiator, to yield low molecular weight polymer. Dilatometric rate comparisons showed that the presence of up to 0.02 wt.-% of radical polymerization inhibitors such as chloranil or diphenylpicrylhydrazyl did not even retard the initial polymerization. The polymers isolated from these reactions could not be separated by solution techniques into their respective homopolymers, so that simultaneous cationic and anionic homopolymerization, as described for vinylidene cyanide-vinyl ether systems,² will not explain the rapid polymerization. It is likely that this is an extreme case of cross-initiation which has been observed in other strongly alternating systems.³ In any case, preparation of castings of such copolymers was impossible; since emulsion or suspension copolymerizations cannot be conducted because of the extreme ease of anionic homopolymerization of MCyA,¹ all evaluations had to be conducted on polymers isolated from solution preparations.

In contrast, copolymerizations with monomers containing electron-withdrawing groups, such as methyl methacrylate (MMA), could be carried out in bulk. Free radical initiators were required, and high molecular weight copolymers could be formed; the properties of certain of these copolymers are discussed below.

Solution Copolymerizations

In contrast to their behavior in bulk, mixtures of MCyA and monomers having negative e values did not spontaneously or thermally polymerize in benzene at 60°C., but required free radical initiators, such as azobisisobutyronitrile (AIBN). Copolymerizations with volatile monomers, such as isobutylene, were carried out by saturating a MCyA-benzene or MCyA-toluene mixture with the gaseous monomer and then bubbling the gas through the mixture. When benzoin and ultraviolet light were used to initiate, copolymers with isobutylene could be prepared at temperatures as low as -15°C.

To determine qualitatively the relative reactivity of MCyA with a large number of monomers, equimolar mixtures were polymerized with AIBN in a mutual solvent (usually benzene) at 60°C. The general observations are subdivided as to the structure of the second monomer.

Allylic Monomers. Allyl acetate, allyl chloride, and allyl phenyl ether copolymerized to give polymers enriched in MCyA and of molecular weights

ca. 10^5 (based on the intrinsic viscosity-molecular weight relationship established for MCyA homopolymer¹). Apparently, degradative chain transfer was not a major factor in these polymerizations.

Olefins. Copolymerization with octene-1 was studied in some detail and is discussed in the Appendix. Other 1-olefins copolymerized similarly, with significant but not equimolar incorporation of the olefin into the copolymer. Isobutylene appeared to form an alternating copolymer, but this was not consistent with the behavior of other 1,1-disubstituted olefins, e.g., purified diisobutylene (2,4,4-trimethylpentene-1) and 2-methylpentene-1, which did not copolymerize well. Olefins with internal unsaturation were unreactive, only MCyA homopolymer being formed. No studies with dienes were made.

Vinyl Esters and Vinyl Halides. Reactivity ratios for vinyl acetate are discussed below. High molecular weight copolymers whose composition tended toward an alternating structure were prepared from vinyl 2-ethylhexoate, isopropenyl acetate, and vinyl benzoate. Vinyl halides could not be incorporated in the few scouting experiments tried, while vinylidene chloride was not examined.

Vinyl Ethers and Vinyl Sulfides. Our results with vinyl ethers did not parallel those reported by Gilbert et al.² for copolymers with vinylidene cyanide. Here only small amounts of comonomer were incorporated, and the conversions were quite low. In contrast, methyl, phenyl, and benzyl vinyl sulfides tended to alternate with MCyA. 1,1-Dibutylthioethylene (ketene dibutyl mercaptal)⁴ and α -ethylthiostyrene,⁵ which were expected to exhibit a very low e value and thus to alternate, gave only traces of polymer.

Styrene. Alternating copolymers were formed with styrene, α -methylstyrene, vinyl toluene, α,p -dimethylstyrene, and α -acetoxystyrene. *trans*-Stilbene and 1,1-diphenylethylene did not alternate with MCyA.

Acrylic Esters. The copolymerization behavior of MCyA with acrylate and methacrylate esters is apparently random, as can be seen from the reactivity ratios discussed below. Copolymers with other monomers of high e values were not studied. Mihail, Lupu, and Dascalu⁶ have reported copolymers with high softening temperatures of MCyA with acrylonitrile; these were prepared with H_2O_2 in emulsion, and an anionic initiation process is suspected.

Copolymerization Parameters

Controlled solution polymerizations were carried out with MCyA and five reference monomers: methyl methacrylate, methyl acrylate, vinyl acetate, styrene, and α -methylstyrene. The results are shown in Table I.

Although the results are generally consistent, we feel that results are more indicative of trends than an accurate set of reactivity ratios. This is due to a variety of experimental factors: difficulty in eliminating anionic initiators for MCyA,¹ difficulty in isolating low conversion polymer from the highly reactive systems, and a correction which had to be applied for all

TABLE I
Solution Copolymerization Parameters for Methyl α -Cyanoacrylate (M_1)

M_2	r_1	r_2	r_1r_2	e_1	$\log Q_1$
Methyl acrylate	1.2	0.1	1.2×10^{-1}	2.1	1.00
Methyl methacrylate	0.25	0.04	1.0×10^{-2}	2.5	1.64
Styrene	0.03	0.01	3.0×10^{-4}	2.1	1.10
α -Methylstyrene	0.001	0.05	5.0×10^{-5}	1.9	-0.49
Vinyl acetate	0.5	0.005	2.5×10^{-3}	2.1	0.43

nitrogen analyses (the homopolymer of MCyA analyzes 4% low for Kjeldahl nitrogen content). We feel it can be concluded that the copolymers with styrene and α -methylstyrene are truly alternating and that the e value for MCyA is about +2.1. The scatter in $\log Q_1$, although large, was not unexpected; Gilbert et al. had reported² a similar scatter for vinylidene cyanide. The experimental data for these systems are not complete enough to test for penultimate unit effects.

BULK PROPERTIES

Random Copolymers with Methyl Methacrylate

The thermal degradation of MCyA homopolymer at temperatures only slightly above its glass temperature¹ led us to a study of MCyA-MMA copolymers. These materials were approximately as thermally stable as the homopolymer, but softened ca. 10–15°C. lower, so that forming operations could be carried out. Other physical properties of the cast sheet were similar to those of MCyA homopolymer,¹ with the copolymer exhibiting slightly higher flexural modulus, flexural strength, and unnotched impact resistance.

Alternating Copolymers with Styrene

The problems in preparing such alternating copolymers in bulk have been discussed; properties of the polymers reported here were obtained on compression molded samples. The Vicat softening points of several of these copolymers approached that of MCyA homopolymer, while the thermal stability was enhanced. Some representative Vicat values for alternating copolymers were: α -acetoxystyrene, 171°C.; α -methylstyrene, 154°C.; styrene, 133°C.; vinyltoluene, 135°C.; α,p -dimethylstyrene, 125°C.; isobutylene, 88°C. Typical Vicat softening points for MCyA homopolymer and MCyA-10% MMA copolymer are 165–69°C. and 150–155°C., respectively. These copolymers were transparent although sometimes yellow.

A brief attempt was made to determine whether the glass transition temperature T_g for alternating copolymers would obey any of the equations⁷ relating T_g for random copolymers to copolymer composition and T_g of the related homopolymers. It is experimentally quite difficult to

choose systems which yield alternating copolymers for which the glass temperature of the corresponding homopolymers can be determined; usually one of the components will not homopolymerize, will yield a crystalline polymer, or (as with MCyA homopolymer) begin to degrade at temperatures near T_g . For this reason, we determined the glass temperature dilatometrically (Table II) for an alternating copolymer of *n*-butyl cyanoacrylate and styrene.

TABLE II
Dilatometric Glass Transition Temperatures for Polymers of
Styrene and Butyl α -Cyanoacrylate

Polymer	T_g , °C.	$d\bar{v}/dt \times 10^4$, cc./g./°C.	
		Above T_g	Below T_g
Butyl α -cyanoacrylate ^a	85	5.1	1.1
Styrene ^b	100	5.5	2.5
Alternating copolymer ^c	84	4.9	2.7

^a Estimated $\bar{M}_v = 250,000$, $[\eta]_{\text{nitromethane}} = 0.72$ dl./g.

^b Data of Fox and Flory.⁸

^c Analyzed as 50 mole-% styrene (40.2 wt.-%); estimated $\bar{M}_v > 10^6$, $[\eta]_{\text{nitromethane}} = 2.5$ dl./g.

Although unfortunately only one composition can be studied for an alternating copolymer, it can be seen that this result does not fit the equation of Wood⁷

$$T_g = A_2/A_1 (T_{g_2} - T_g) c_2 / (1 - c_2) + T_{g_1}$$

unless a high negative value of A_2/A_1 is taken. Not enough data are available to suggest how the partial specific volumes for such copolymers should be treated. An apparently alternating copolymer of *n*-butyl α -cyanoacrylate and *N*-vinylpyrrolidone exhibited a T_g of 94°C., which also deviates considerably from that predicted from the T_g values of the homopolymers, polyvinylpyrrolidone having a T_g of ca. 145°C.

THERMAL AND IRRADIATION DEGRADATION

The random copolymers with MMA behaved similarly to the MCyA homopolymer studied earlier,¹ with a rapid drop in molecular weight and a relatively small weight loss when heated in air above 180°C. Use of stabilizers which are effective for MMA homopolymers did not result in copolymer of better stability.

The alternating copolymers were more resistant to thermal degradation than the MCyA homopolymer. The decrease in molecular weight and the weight loss for a MCyA-styrene copolymer after heating 2 hr. in air at 200°C. was about that found when homopolymer is heated 2 hr. at 180°C. Copolymers with vinyltoluene and with methylstyrene (mixture of *o*- and *p*-isomers) crosslinked on heating in air to 250°C.; this effect was not found

on heating *in vacuo*. The behavior *in vacuo* (little monomer liberated, continuous decrease in intrinsic viscosity of residual polymer) suggests random scission with little chain unzipping for these alternating copolymers. No effort has been made to study stability of the copolymers in solution. Many of these results are similar to the enhanced stability found for vinylidene cyanide alternating copolymers relative to the homopolymer.²

The MCyA-MMA random copolymer degraded on exposure to 10 Mrep of γ -irradiation at 40°C. The intrinsic viscosity of the polymer was lowered, and the polymer was less stable to subsequent thermal degradation. On exposure to a similar radiation dose, an alternating copolymer with isobutylene decreased in viscosity, while copolymers with vinyltoluene and with styrene were insolubilized.

EXPERIMENTAL

Methyl α -cyanoacrylate and *n*-butyl α -cyanoacrylate were prepared by the method of McKeever.⁹ The butyl ester boiled at 73.5°C./1.6 mm., n_D^{25} 1.4409. Reference monomers (styrene, α -methylstyrene, vinyl acetate, methyl methacrylate, methyl acrylate) were the best commercial grade available; they were washed, carefully dried, and redistilled shortly before use. Other monomers mentioned in the text were dried and redistilled, except for gaseous monomers which were used directly. In the cases reported here, there was apparently no difficulty with cationic polymerization of the second monomer induced by the boron trifluoride-acetic acid stabilizer present in the MCyA. Reagent grade benzene was used as solvent for most copolymerizations.

For bulk copolymerizations, all reactants except MCyA were weighed and mixed in a dry box under nitrogen, MCyA added from a pipet, the mixture rapidly reweighed and placed in a bath at the desired temperature. Degassing was difficult, and trial experiments indicated traces of oxygen to have little effect on the copolymerization. Dilatometric polymerizations were made by degassing MCyA, freezing this monomer, adding a degassed mixture of inhibitor (if used) and second monomer, refreezing, reevacuating, and adding mercury to the frozen mixture.

Solution copolymerizations were conducted in benzene at 60°C. with azobisisobutyronitrile as initiator. Anhydrous diethyl ether was used as precipitant; after thorough washing to remove residual monomers, the polymers were reprecipitated from chloroform or nitromethane solution into methanol.

Kjeldahl microdeterminations of nitrogen content were used to determine reactivity ratios. A 4% correction was arbitrarily applied in all cases, as the homopolymer consistently analyzed 4% lower than theoretical.

Physical properties were measured on cast sheet for the MCyA-MMA copolymers and on disks molded on a Carver press at 175°C. and 4000 psi for the alternating copolymers. Glass transition temperatures were measured dilatometrically by standard techniques¹⁰ with the use of mercury as the

confining liquid. Intrinsic viscosities were measured in nitromethane at 30°C. Thermal degradation experiments were conducted in a circulating air oven at constant temperature. γ -Irradiations were conducted at the Co⁶⁰ source of the University of Pennsylvania.

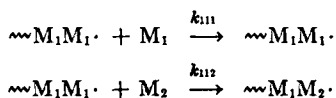
APPENDIX

Copolymerization of Methyl α -Cyanoacrylate with Octene-1

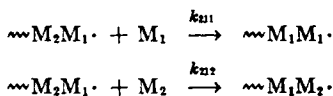
The enhanced reactivity of MCyA led us to hope that copolymerization with a simple olefin might serve to establish Q and e parameters for that olefin; such parameters are not known exactly because of the extreme difficulty of incorporating such olefins into free-radical polymers. Copolymerizations were carried out in sealed evacuated ampules with benzene as solvent (the monomers are immiscible) and AIBN as initiator at 60°C. Phillips Petroleum octene-1 of 99.67% purity was used. Polymers were precipitated into ether.

Calculation of the desired parameters was not accomplished because of the difficulty in assigning exact Q and e values for the MCyA reference monomer. Moreover, it was noted that negative values for r_2 (octene) were obtained when either the differential or integrated forms of the standard copolymerization equations were used. The equations for the penultimate unit effect¹¹ were applied to this system; these equations are applicable only to low conversion polymers and it was, therefore, necessary to approximate certain initial values for polymers from initial ratios high in MCyA. This was done by a method of successive approximations involving an IBM computer programmed to calculate copolymer compositions as a function of conversion.

If we accept the assumptions that (1) the 4% correction should be applied to all Kjeldahl nitrogen analyses, (2) the isolation procedure used recovered all polymer formed, and (3) that no anionic polymerization occurred, then the best results calculated from a Fineman-Ross plot for a "standard" copolymerization are: r_1 (MCyA) = 0.63 ± 0.06 ; r_2 (octene) = -0.17 ± 0.04 . When the Barb¹² form of the penultimate unit equation is applied (in which it is assumed that $r_2 = r_2' = 0$, i.e., that polymer radicals terminating in octene units cannot add octene monomer), then $r_1 = 0.27 \pm 0.04$ and $r_1' = 1.66 \pm 0.11$. Indicating MCyA as M_1 and octene as M_2 , the pertinent equations are:



where $r_1 = k_{111}/k_{112}$, and



where $r_1' = k_{211}/k_{212}$. These results indicate that there is an added repulsion between the adding MCyA monomer and the penultimate MCyA unit not found when the penultimate unit is octene. Such effects have previously been found with other nitrile-containing monomers, but this effect is larger than that found for vinylidene cyanide, a monomer of higher e value which might be expected to exhibit more electrostatic repulsion.¹³ However, the penultimate unit effect in that case is found in the reaction of the polymeric radical bearing the second unit with vinylidene cyanide, as vinylidene cyanide cannot add to its own radical.

Penultimate unit effects are masked in the reaction of MCyA with most monomers because r_2 is not zero in most cases, and so it is very difficult to calculate such variations by involved curve fitting.

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Résumé

La copolymérisation de l' α -cyanoacrylate de méthyle avec cinq monomères de référence donne des valeurs de $e = +2.1$ et de $\log Q = 0.65$ avec beaucoup de dispersion dans la dernière valeur. Des copolymères alternés sont formés par copolymérisation avec des monomères possédant un $e = -0.8$ ou plus petit. Une copolymérisation en bloc avec de tels monomères ne peut pas se faire de même qu'une polymérisation rapide non catalysée a lieu par mélange même à 0°. Des copolymères statistiques avec le méthacrylate de méthyle peuvent être préparés en bloc; ceux obtenus avec environ 10% de méthacrylate de méthyle ont des propriétés physiques semblables à l'homopolymère de l' α -cyanoacrylate de méthyle, excepté que la température de la chaleur de distortion est abaissée de 10–15°C. Les copolymères alternés sont plus stables thermiquement que les copolymères statistiques. Les valeurs de la température vitreuse pour les copolymères alternés ne semblent pas en accord avec les valeurs prévues à partir des équations pour les copolymères statistiques.

Zusammenfassung

Die Kopolymerisation von Methyl- α -Cyanacrylat mit fünf Referenzmonomeren liefert die Werte $e = +2,1$ und $\log Q = 0,65$, wobei letzterer Wert stark streute. Mit Monomeren mit $e = -0,8$ oder kleiner werden alternierende Kopolymere gebildet. Mit diesen Monomeren konnte keine Kopolymerisation in Substanz erreicht werden, da sogar bei Mischung bei 0° eine schnelle nicht katalysierte Polymerisation auftritt. Statistische Kopolymere mit Methylmethacrylat konnten in Substanz dargestellt werden; diejenigen mit ca. 10% Methylmethacrylat besaßen ähnliche physikalische Eigenschaften wie das Homopolymere von Methyl- α -Cyanacrylat mit der Ausnahme, dass die Hitzeverformungstemperatur um $10-15^\circ\text{C}$ erniedrigt war. Die alternierenden Kopolymeren waren thermisch stabiler als die statistischen Kopolymeren. Die Werte der Glasumwandlungstemperatur für alternierende Kopolymere scheinen nicht mit den aus Gleichungen für statistische Kopolymere abgeleiteten Werten übereinzustimmen.

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