# Methyl α-Cyanoacrylate. I. Free-Radical Homopolymerization*

A. J. CANALE, W. E. GOODE, J. B. KINSINGER,† J. R. PANCHAK, R. L. KELSO, and R. K. GRAHAM‡

*Research Division, Rohm & Haas Company, Bristol, Pennsylvania*

The preparation of high polymers of methyl α-cyanoacrylate by free-radical initiation does not seem to have been adequately described in the literature. Procedures for the preparation of the monomer,[1,2] stabilization against anionic polymerization,[2] and some properties of the bulk polymer[1] have appeared in the patent literature. A discussion of the chemistry of cyanoacrylate monomers as adhesives has appeared.[3] With the exception of a recent study by Mihail, Lupu, and Dascalu,[4] most of the properties appear to have been measured on low molecular weight materials initiated by water, alcohols, and other weak bases. Such behavior in the presence of weak bases is similar to that of vinylidene cyanide[5] and nitroethylene.[6] Unlike these monomers, however, methyl α-cyanoacrylate (hereafter abbreviated as MCyA) polymerizes readily by free-radical techniques to form high molecular weight polymer. In the present communication we report some observations on the free-radical homopolymerization of MCyA and some properties of the polymer in bulk and in solution. A subsequent paper will discuss the copolymerization behavior of this interesting monomer.

## POLYMERIZATION BEHAVIOR

### Anionic Polymerization

As has been disclosed[1,2] and as might be expected from its similarity to vinylidene cyanide, MCyA is readily polymerized by traces of base, even by materials as weakly basic as alcohols and water. [Coover et al.[3] have shown that such facile anionic polymerization occurs with monomers possessing two groups exhibiting strong electromeric (-E) effects.[7] Similar behavior was noted[8] for purified dimethyl methylenemalonate,[9] $CH_2{=}C(CO_2CH_3)_2$.]

When the monomer is suitably inhibited with a Lewis acid against anionic polymerization and when precautions are taken against extraneous moisture (such as using acid-washed and carefully dried equipment and conducting all handling operations in a dry box), reproducible results can be obtained in free-radical polymerizations.

## Bulk Free-Radical Polymerization

Establishment of the free-radical nature of the polymerization was based on the observations that polymerization could be initiated with such common radical initiators as azobisisobutyronitrile (AIBN) and could be inhibited with diphenylpicrylhydrazyl. The rate data also appear to support a free-radical polymerization.

Precise rate data are very difficult to obtain, even when anionic polymerization is suppressed, as an almost immediate acceleration of rate occurs
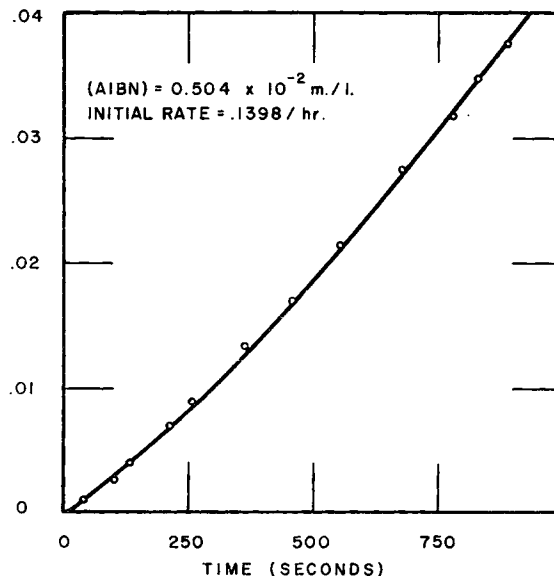


Fig. 1. Rate of bulk polymerization of methyl α-cyanoacrylate at 60°C., initiated by azobisisobutyronitrile.

at low conversion. This effect is similar to that found for methyl acrylate,[10] although the auto-acceleration is detected here at even lower conversions. Some turbidity is noticed throughout the polymerization, but no settling out of polymer was found; the polymer formed at high conversions is optically clear. This behavior is somewhat similar to that of methacrylonitrile in bulk.[11]
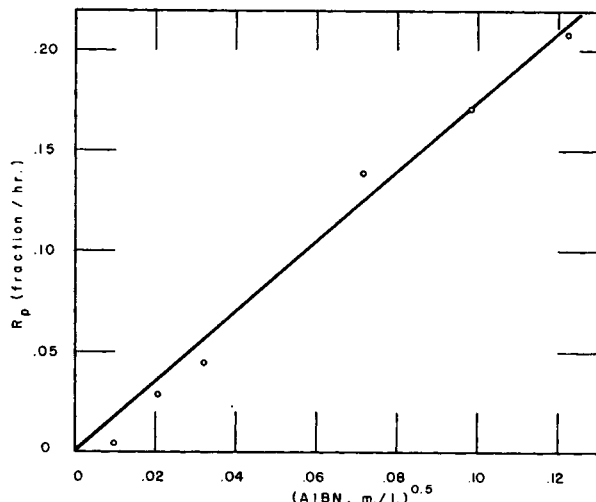


Fig. 2. Rate of bulk polymerization of methyl α-cyanoacrylate at 60°C. as a function of initiator concentration.

The data from a typical dilatometric polymerization are shown in Figure 1; extrapolation to initial rate was made from times of less than 200 sec. A duplicate polymerization was performed at the same time with no AIBN present, and the rate of this control was subtracted from the overall rate to obtain the AIBN-initiated rate to compensate for any spurious anionic or free-radical reactions. It is realized that error could be introduced because of expansion of the confining liquid under nonsteady-state conditions[12] and also because the rate of the "control" is competitive with the AIBN-initiated reaction, so that the corrected rate is a relatively small difference between relatively large numbers. A series of these measurements was applied to the determination of the rate-initiator concentration relationship, which is shown in Figure 2 to be: rate (%/hour) = 175 [AIBN]$^{0.5}$; rate (fraction/sec.) = 4.86 × 10$^{-4}$[AIBN]$^{0.5}$ = $R_p$/[M]. From this relationship, from the known values[13] for the decomposition of AIBN at 60°C. (1.1 × 10$^{-5}$ sec.$^{-1}$) and arbitrarily assuming 100% efficiency of initiation, $k_p^2/k_t$ is calculated as 0.021 l./mole/sec. Although this calculation requires several approximations, it allows a comparison

(Table I) of this value with those for several other common monomers.

TABLE I
Comparison of $k_p^2/k_t$ Values of Various Vinyl Monomers at 60°C.

| | $k_p^2/k_t \times 10^2$, l./mole/sec. | Reference |
|---|---|---|
| Vinylidene cyanide | —[a] | 5 |
| Styrene | 0.116 | 14 |
| Acrylonitrile | 0.491[b] | 15 |
| Methacrylonitrile | 0.697[b] | 15 |
| Methyl methacrylate | 1.44 | 16 |
| Methyl α-cyanoacrylate | 2.1[c] | This work |
| Vinyl acetate | 18.5 | 16 |
| Methyl acrylate | 106.0 | 16 |

[a] Does not appear to form homopolymer with free-radical initiation.

[b] Measured in dimethylformamide solution.

[c] Assumes 100% efficiency of initiation.

It can be seen that MCyA is quite unlike vinylidene cyanide in its free-radical homopolymerization behavior. Examination of models suggests a lower degree of electrostatic hindrance for addition of MCyA to its own polymeric radical relative to vinylidene cyanide, but the striking difference in behavior is not obviously explained.

The relatively high value of $k_p^2/k_t$ may be related to a low value of $k_t$. Mutual electrostatic and steric repulsion would make mutual combination of radicals relatively unlikely. Termination by disproportionation would involve abstraction of a hydrogen atom from the ester methyl group (unlikely) or from a β-carbon; examination of models suggests that abstraction of hydrogen from the β-carbon is much more hindered than that from a methyl group such as that in methyl methacrylate.

## Inhibition, Branching, and Chain Transfer

No detailed study of the inhibition of free-radical polymerization of MCyA has been made. Many of the common inhibitors, especially those which function as antioxidants, contain basic functional groups which initiate anionic polymerization of MCyA. Diphenylpicryhydrazyl and benzoquinone are relatively effective inhibitors. Furfurylidene malononitrile, a very effective inhibitor for styrene[17] and a relatively effective inhibitor for methyl methacrylate[18] and methyl acrylate,[19] acts only as a retarder of polymerization in this system. An effective inhibitor of MCyA would be expected to act as an electron donor, so that a

contribution to the transition state could be made by resonance forms of the type

$$\begin{array}{c} CN \\ | \\ -CH_2-C:^{\delta-}---(Inhibitor)^{\delta+} \\ | \\ COOCH_3 \end{array}$$
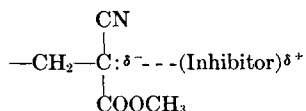
with a consequent lowering of the activation energy.[20] Furfurylidene malononitrile would be expected to act as an electron acceptor in such systems[18] and so would be much less effective.

Branching by chain transfer with polymer is unlikely with MCyA, since there are no labile hydrogen atoms in the polymer. No crosslinked polymer has ever been detected, even in high conversion polymerizations, but no attempt has been made to detect low degrees of branching. Synthesis of pure model compounds for chain transfer studies has proved difficult.

Attempts to regulate the molecular weight of bulk or solution polymerizations with dodecyl mercaptan indicated that little change was effected. Also, conversions seemed to be somewhat higher in the presence of mercaptan. It is conceivable that the mercaptan is capable of acting as a weak anionic initiator. Mercaptans would not be expected to be very effective transfer agents in the radical polymerization of MCyA, since polar contributions to the transition state are less favored than in the case of styrene;[21] however, it was unexpected that essentially no control could be achieved.

### Solution Polymerization

An attempt to study polymerization in solution to minimize the autoacceleration effect found in bulk was unsuccessful when benzene was used as a solvent, since the polymer precipitated as a highly swollen gel. Many of the solvents in which homogeneous polymerizations could be conducted are extremely difficult to obtain completely free of water or other ionic initiators. Near the completion of this study, it was found that AIBN-initiated solution polymerizations could be conducted in carefully purified isobutyronitrile or nitromethane, but no kinetic data were obtained in these solvents.

Mihail et al.[4] have described the emulsion polymerization of cyanoacrylate esters initiated with hydrogen peroxide in the absence of emulsifying agent. The molecular weight was reported to decrease with increasing temperature. The extreme sensitivity of MCyA to even traces of water

strongly suggests that these polymerizations were not free-radical, but anionic in nature.

### SOLUTION PROPERTIES

Solvents for the homopolymer include propionitrile, pyridine, nitroethane, nitromethane, acetonitrile, dimethylformamide, ethylene carbonate, succinonitrile, and butyrolactone. Swelling ratios in these solvents were measured on polymer crosslinked with a small amount of ethylene glycol dimethacrylate; a rough estimate of the square root of the cohesive energy density from these data gives a value of ca. 14.5, relatively close to that for polyacrylonitrile. Many of the above solvents are also solvents for polyacrylonitrile. Polymers of MCyA are insoluble in alcohols, which indicates the absence of strong hydrogen bonding. The homopolymer is also insoluble[5] in common aromatic solvents (benzene, toluene), ketones (acetone, methyl ethyl ketone), and chlorinated solvents (chloroform, ethylene dichloride).

Polymers were purified for analysis by dilution with purified nitromethane and precipitation in the nonsolvent, diethyl ether. Anhydrous ether was used to prevent inadvertant polymerization of remaining monomer. After thorough washing with ether to remove monomer, the polymer was redissolved in nitromethane and reprecipitated into ether or methanol containing a little hydrochloric acid.

Preliminary data have been obtained on the intrinsic viscosity–molecular weight relationships for MCyA homopolymer in acetonitrile (a poor solvent) and nitromethane (a good solvent). Measurements were carried out at 30°, which is below the theta temperature for this polymer in acetonitrile. The data for four whole polymers give the relationships:

$$[\eta] = 6.43 \times 10^{-5} M_w^{0.77} \text{ (nitromethane, 30°,}$$

$$\text{MW range } 10^6 \text{ to } 5 \times 10^6)$$

$$[\eta] = 8.45 \times 10^{-4} M_w^{0.45} \text{ (acetonitrile, 30°,}$$

$$\text{MW range } 5 \times 10^3 \text{ to } 3 \times 10^5)$$

It is hoped to publish more details on the dilute solution behavior at a later date. The present relationships are useful in showing that high molecular weight polymer is formed with radical initiators.

Solutions of MCyA polymer in dimethylformamide or dimethyl sulfoxide exhibited a decrease in intrinsic viscosity on long standing at room tem-

perature or on heating. This behavior is reminiscent of that observed for poly(vinylidene cyanide) in the presence of water and bases.[5]

## BULK PROPERTIES

The homopolymer must be prepared from very pure monomer to give clear, transparent sheet castings; traces of impurities can lead to yellowing of the material. Molding of samples for physical testing is difficult because of the thermal degradation discussed below.

Dilatometric measurement of the glass temperature could not be accomplished because of degradation at temperatures only slightly above the glass temperature. From the Vicat softening point and A.S.T.M. heat distortion measurements, the glass temperature was estimated to be $165°C. < T_g < 170°C.$, which agrees well with earlier results.[22]

### TABLE II
Physical Properties of High Molecular Weight
Poly(methyl α-Cyanoacrylate)

| | No. 1 | No. 2 | No. 3 | Plex II[a] |
|---|---|---|---|---|
| Heat distortion temp., °C., at 264 psi (ASTM-D-648-56) | 163[b] | 157[b] | 160[b] | 96[b,c] |
| Impact strength, Izod, unnotched, $1/2 \times 1$ in. section (ASTM-D-256-56) | 5.8 | 6.3 | 5.6 | 7.0[d] |
| Flexural strength, psi (ASTM-D-790-49-T) | 16,500 | 15,100 | 17,700 | 16,000 |
| Modulus in flexure, psi | 554,000 | 557,000 | 530,000 | 450,000 |
| Deflection at break, in. | 0.46 | 0.45 | 0.49 | 0.6 |
| Reduced specific viscosity, dl./g.[e] | 1.8 | 2.5 | 2.0 | — |

[a] Average values not intended for specification purposes.

[b] Conditioned 48 hr. at 50°C.

[c] Not annealed; value increased ca. 15° on annealing.

[d] Estimated from Charpy unnotched on $1/2 \times 1/2$ in. section.

[e] In nitromethane at 25°C. at 2 g./l.

The cast sheet exhibits physical properties comparable with other high molecular weight thermoplastic materials such as poly(methyl methacrylate). Some typical properties of our best preparations are shown in Table II, where they are compared with typical data for Plexiglas II.

## THERMAL AND IRRADIATION DEGRADATION

On heating in air above 180°C., the homopolymer of MCyA yellows and bubbles. Some monomer is liberated, and the intrinsic viscosity of the residue drops sharply. Under these conditions, most of the relatively nonvolatile monomer cannot escape and is repolymerized to low molecular weight material. The actual weight loss is low. A few *in vacuo* experiments indicated the decrease in molecular weight to be less pronounced, but the amount of volatile material increased sharply.

The relative ease of thermal depolymerization has been utilized in the synthesis of MCyA monomer from low polymer.[1,2] Attempts to add stabilizers or to vary the nature of the end groups have been unsuccessful in preventing this degradation. Whether initiation of depolymerization occurs randomly or preferentially at weak links has not been determined; possible sources of weak links might be tail-to-tail placement caused by termination of polymerization by combination or ketimine links from polymerization through the nitrile group. Such ketimine links, previously reported for polymethacrylonitrile,[23] could not be detected by ultraviolet spectroscopy.

Gamma irradiation *in vacuo* of MCyA homopolymer causes a decrease in molecular weight which appears to be proportional to dose. In Figure 3 are plotted reciprocal viscosity-average molecular weights for MCyA and MMA homopolymers as a function of irradiation time. From the relative slopes of these lines and the known energy requirements for irradiation degradation
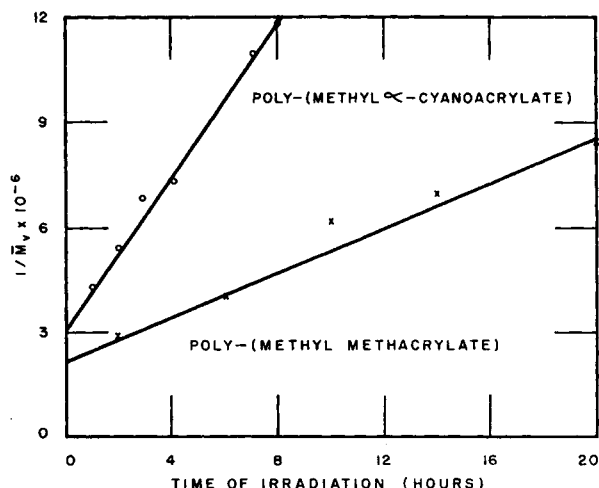


Fig. 3. Reciprocal viscosity-average molecular weight, $1/\bar{M}_v$, plotted against time of irradiation for poly(methyl α-cyanoacrylate) and poly(methyl methacrylate).

of poly(methyl methacrylate) (60 e.v. per main-chain scission),[24] poly-MCyA appears to require only ca. 18 e.v. per main-chain scission. Not enough data are available to show that some concurrent crosslinking is not occurring; as Shultz has pointed out,[24] it is possible that such a decrease in apparent viscosity-average molecular weight can be found with some crosslinking also occurring. This behavior would be unexpected, however, in view of the rather general rule that polymers of backbone structure —$CH_2$—CXY— only degrade.[25]

## EXPERIMENTAL

Monomer of high purity was prepared by the method of McKeever,[26] in which the condensate of formaldehyde and methyl cyanoacetate is treated with acetic anhydride to remove water liberated in the cracking of the condensate. The monomer had the following properties: m.p. 1°C., b.p. 46°C. (1.5 mm.), $n_D^{25}$ 1.4431, $d_4^{25}$ 1.100 g./ml., $d^{60}$ 1.067 g./ml. The monomer was inhibited against anionic polymerization with boron trifluoride–acetic acid complex and stored in a refrigerator in polyethylene bottles.

Rates of polymerization were followed at 60°C. dilatometrically, mercury being used as the confining liquid. The density of the polymer was 1.304 g./ml. at 25° and 1.289 g./ml. at 60°, and the contraction on polymerization was 18.7 ml./mole. In many of the polymerizations, a second dilatometer containing no initiator was filled and degassed at the same time. Rates of both polymerizations were measured and the rate of polymerization of the control subtracted from the overall rate.

Reagent grade nitromethane and anhydrous diethyl ether were used as diluents and precipitants. Dodecyl mercaptan was redistilled before use. Diphenylpicrylhydrazyl and furfurylidene malononitrile were supplied by Dr. J. L. Kice.

The intrinsic viscosity measurements were determined with a Ubbelohde-type viscometer at 30°C. Light-scattering measurements were determined with a Brice-Phoenix light scattering photometer at 30°C.

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## Synopsis

Methyl α-cyanoacrylate, when suitably inhibited by Lewis acids against anionic polymerization, can be polymerized readily with free-radical initiators to form hard, clear, high molecular weight polymers. The ratio of $k_p^2/k_t$ is approximately 0.021 at 60°C. if 100% efficiency of initiation by azobisisobutyronitrile is assumed. Acceleration occurs at very low conversion to polymer during bulk polymerizations. The homopolymer is thermally unstable at temperatures only slightly above the glass temperature (estimated to be 165–170°C.). Degradation of the polymer under gamma irradiation is pronounced, only 18 e.v. being required per main-chain scission.

## Résumé

L'α-cyanoacrylate de méthyle, lorsqu'il est convenablement inhibé par les acides de Lewis vis-à-vis de la polymérisation anionique, peut être rapidement polymérisé par des initiateurs radicalaires pour donner un polymère dur, clair et de haut poids moléculaire. Le rapport $k_p{}^2/k_t$ est approximativement de 0,021 à 60°C si l'on admet 100% d'efficacité d'initiation par l'azobis(isobutyronitrile). L'accélération a lieu a des tres faibles degrés de conversion durant la polymérisation en bloc. L'homopolymère n'est thermiquement instable qu'à partir d'une température légèrement supérieure à la température de transition vitreuse (estimée à 165–170°C). La dégradation du polymère par irradiation gamma est prononcée et elle ne nécessite que 18 électron-volts par scission de chaîne.

## Zusammenfassung

Methyl-α-cyanoacrylat, das durch die Anwesenheit von Lewis-Säuren gegen anionische Polymerisation entsprechend geschützt ist, kann mit radikalischen Startern leicht zu harten, klaren, hochmolekularen Polymeren polymerisiert werden. Das Verhältnis $k_p{}^2/k_t$ beträgt unter Annahme einer 100% Starterausbeute mit Azo-bis-isobutyronitril bei 60°C etwa 0,021. Bei der Polymerisation in Substanz tritt bei sehr niedrigem Umsatz eine Reaktionsbeschleunigung ein. Das Homopolymere ist bei Temperaturen, die nur schwach oberhalb der Glasumwandlungstemperatur (zu 165–170°C bestimmt) liegen, thermisch instabil. Der Abbau des Polymeren unter Gammabestrahlung ist erheblich; es sind nur 18 Elektronvolt zur Spaltung der Hauptkette erforderlich.