

Degradation and Stabilization of Polycyanoacrylates

DOUGLAS R. ROBELLO, TERESA D. ELDRIDGE, MICHAEL T. SWANSON

Eastman Kodak Company, Research Laboratories, Rochester, New York 14650-2116

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ABSTRACT: Polycyanoacrylates were found to be inherently unstable. Even in the absence of a deliberately added strong base, their molecular weights decreased drastically on standing in solution in accord with observations by Ryan and McCann (*Makromol Chem Rapid Commun* 1996, 17, 217). The initial high molecular weight polymer disappeared over the course of a few hours in solution and was replaced by a much lower molecular weight material. For polymers made by anionic polymerization, the entire sample degraded, but for polymers made by free-radical polymerization, only a portion of the sample was affected. This behavior was consistent with the mechanism proposed by Ryan and McCann, in which the polymer chains are in dynamic equilibrium with their monomers and the polymer degrades from its chain terminus. Surprisingly, the degradation in molecular weight even occurred slowly in the solid state. The degradation was inhibited by acids and could be prevented by free-radical copolymerization with small amounts of more stable monomers. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 4570–4581, 1999

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INTRODUCTION

In a recent communication, Ryan and McCann¹ described rapid changes in the molecular weight (M_r) of poly(butyl cyanoacrylate) (PBCA) when it was treated in solution with a strong base, tetrabutylammonium hydroxide. These authors suggested that the added base deprotonated the chain end, leading to the rapid depolymerization of the polymer backbone, followed by the simultaneous repolymerization of the liberated monomer to produce a “daughter” polymer of much lower molecular weight.

Their publication prompted us to describe our own parallel studies of cyanoacrylate polymers in which we reproduced these molecular weight

changes and obtained evidence in support of the mechanism proposed by Ryan and McCann.¹ Moreover, our experiments indicated that this equilibration behavior is even more general than previously indicated and affects similar polymers made with nucleophilic initiators and (to a lesser extent) those made with free-radical initiators. We discovered that added base is not necessary; adventitious base is sufficient to promote molecular weight degradation. Unexpectedly, the depolymerization–repolymerization reaction was observed even in the solid polymer. We also describe herein a simple method for producing polycyanoacrylates (PCAs) that are immune to this degradation reaction.

Background

Cyanoacrylates (**1**) are remarkable compounds. Best known as “instant adhesives” or “super glues,” they were discovered serendipitously by

Correspondence to: D. R. Robello (E-mail: drobello@kodak.com)

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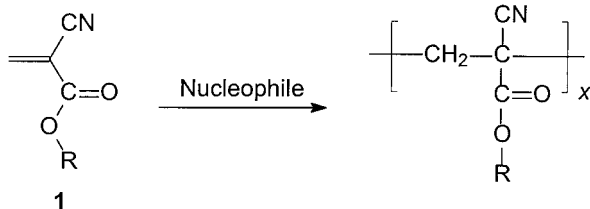


Figure 1. Anionic polymerization of cyanoacrylates.

Coover² in 1953 at what was then the Tennessee Eastman Chemicals Division of the Eastman Kodak Company. The mechanism of adhesive action is anionic polymerization (Fig. 1). The monomers are polymerized rapidly on contact with nucleophiles, including even water at a sufficiently high concentration. As many who have worked with these compounds can attest, the nucleophiles present in skin proteins are especially good initiators. Because of their rapid bonding of tissue, cyanoacrylates also have been investigated as surgical adhesives.³

The details of the mechanism of polymerization of cyanoacrylates by nucleophiles have been studied extensively by Pepper and coworkers.^{4–13} These researchers published evidence that, for uncharged nucleophiles such as tertiary amines and phosphines, the polymerization proceeds via a macrozwitterion and has living character (Fig. 2). With amines, however, the rate of Michael addition of the initiator to the monomer is slow compared to the rate of propagation. Pepper⁹ called this situation a “slow-initiation, no termination mechanism.” Most of the amine remains unreacted after polymerization is complete (this result has implications on the degradation of the polymer and is discussed later). Because of the unusual kinetics with amine initiators, there is not the expected correspondence between the amount of initiator and the polymer molecular weight as is observed for true living polymerizations. Nonetheless, tertiary phosphines are much more rapid initiators of cyanoacrylates, and these systems exhibit the hallmarks of ideal living polymerization. Note that, in all cases, the propagation step is extremely rapid and has an unusually low activation energy. For example, Johnston and Pepper¹³ found that cooling the reaction to -95°C only reduced the rate by half. Very high molecular weights, up to 10^6 , typically are obtained by anionic polymerization.

When uncharged nucleophilic initiators such as tertiary amines or phosphines are employed, the polymerization perhaps is described better as

zwitterionic, although the only formal difference between this mechanism and simple anionic polymerization is that the counterion is bound covalently to the origin of the polymer chain. We refer to this class of polymerization as *anionic* because the propagation step takes the form of the addition of an anionic chain end to a Michael acceptor monomer, regardless of counter ion.

Cyanoacrylates also can be polymerized by using conventional free-radical initiators.¹⁴ In this case, it is common to include some acid in the reaction mixture to suppress accidental anionic polymerization. For free-radical polymerization, the propagation step is probably much slower than for anionic polymerization, and the corresponding molecular weights are generally lower. Free-radical polymerization is a viable method for synthesizing PCAs; however, the predominate worldwide use of these compounds is as adhesives where anionic polymerization is the operative mechanism.

MOLECULAR WEIGHT MEASUREMENTS

Before studying the degradation behavior of PCAs, we needed a reliable means of assaying their molecular weights, especially because relatively rapid degradation can occur in solution under certain circumstances (discussed later). Pepper¹¹ wrote the following:

“A problem of a different kind is the difficulty of finding suitable solvents, especially for molecular weight determination of the polymers. The strongly polar solvents, nitromethane, acetonitrile and dimethylformamide, dissolve the polymers from methyl, ethyl and *n*-butyl esters (PMCA, PECA, PBCA) but in various cases are either known or suspected to cause degradation. Solutions of high molecular weight PECA in THF show remarkable viscosity and GPC anomalies. (p 67)”

Related problems were encountered by Guthrie et al.,¹⁵ who tested the molecular weight of an ethyl cyanoacrylate (ECA) adhesive after periods

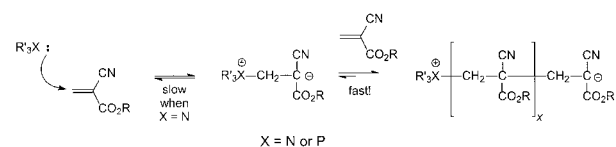


Figure 2. Mechanism of the anionic polymerization of cyanoacrylates by nucleophiles.

of heating. These researchers found a gradual decrease in tensile shear strength of the PCA bond between steel plates over 2 days at 90 °C. Because they attempted to perform size exclusion chromatography (SEC) of the PCA in tetrahydrofuran (THF), their measurements were confounded by artifacts, and they were unable to resolve a substantial low molecular weight fraction. They concluded, possibly erroneously, that the observed decrease in bond strength was not caused by molecular weight degradation.

We found that the degradation of PCAs in solution could be inhibited by the addition of acid (discussed later). Fortunately, an acidic eluent for SEC was available from previous work by Mourey and coworkers,^{16–17} namely 20/80 dichloroacetic acid/dichloromethane containing 0.01 M of ammonium acetate. Not only were all of the PCAs that we studied soluble in this aggressive medium, but no change in the molecular weight of the PCAs occurred in solution, and the SEC was free from artifacts caused by specific interactions between the PCAs and column packing. Significantly, we successfully observed lower molecular weight species without difficulty.

SYNTHESIS

The PCAs for this study were synthesized either by anionic polymerization (trialkylamines, triphenyl phosphine, or methyl magnesium iodide as initiators) or by free-radical polymerization [azobisisobutyronitrile (AIBN) as initiator]. The polymers were precipitated into excess nonsolvent and dried thoroughly *in vacuo* at room temperature. Table I shows the structures of the PCA homopolymers used in this study, along with indexing information.

DEGRADATION OF ANIONIC PCAS

Molecular Weight Studies

As synthesized by anionic polymerization, PCAs possess very high molecular weights (typically several hundred thousands). However, we found to our great surprise at the time that the molecular weight rapidly degrades simply on dissolution in ordinary solvents such as acetonitrile or acetone. For example, Figure 3 shows SEC results for a sample of poly(ethyl cyanoacrylate) (PECA; made with triethylamine as the initiator, then

isolated and dried) dissolved in acetonitrile, held at room temperature, and sampled periodically. Even more remarkable was the nature of the degradation. Rather than gradual shifting to a lower molecular weight, the original high molecular weight material slowly disappeared and was replaced by a much lower molecular weight fraction (typically 10,000–40,000 g/mol). This daughter fraction gradually increased slightly in molecular weight as the equilibration proceeded; however, no material of intermediate size could be detected. Once the high molecular weight material had disappeared, there were no further changes in the low molecular weight fraction, even after prolonged incubation. Similar results were obtained by Ryan and McCann,¹ in our experiments, however, no additional base was added to the samples.

We deconvoluted the SEC curves for the samples incubated for 10 and 55 min, using Gaussian functions for peak fitting (Figure 4). This analysis indicated that the samples were 42 and 47% degraded, respectively. We were unable to fit the curves taken at later times because the peak for the remaining high molecular weight material was too small for the numerical algorithm to locate properly.

The molecular weight distributions of the two fractions in the bimodal samples and fully degraded material were fairly narrow, with a polydispersity of approximately 1.5.

We also found that the rate of equilibration decreases with different initiators in the sequence triethylamine > triphenyl phosphine > methyl magnesium iodide. This observation is in accord with the mechanism proposed by Ryan and McCann.¹ Inevitably, some residual initiator or its by-product (magnesium hydroxide in the case of Grignard reagents) can be entrapped in the polymer upon isolation. Stronger bases are expected to deprotonate the dormant chain ends more readily.

Remarkably, this degradation of molecular weight occurred even in the solid state, albeit at a greatly diminished rate. Figure 5 shows the change in the molecular weight of a sample of triethylamine-initiated poly(2-methoxyethyl cyanoacrylate) (PMECA) that occurred after storage for 8 months as a dry powder in a sealed bottle at room temperature.

Clearly, the degradation of molecular weights is substantial and must impact the physical properties of the polymers. For example, PCAs are reputed to have anomalously low solution viscos-

Table I. Cyanoacrylate Monomers and Homopolymers

Polymer	Monomer		Homopolymer	
	Code	CAS Reg. No.	Code	CAS Reg. No.
$\left[\text{CH}_2 - \underset{\begin{array}{c} \text{CN} \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}}{\text{C}} \right]_x$	ECA	7085-85-0	PECA	25067-30-5
$\left[\text{CH}_2 - \underset{\begin{array}{c} \text{CN} \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}}{\text{C}} \right]_x$	BCA	6606-65-1	PBCA	25154-80-7
$\left[\text{CH}_2 - \underset{\begin{array}{c} \text{CN} \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}}{\text{C}} \right]_x$	MECA	27816-23-5	PMECA	36343-78-9

ities, a characteristic that we now suspect is caused by the rapid degradation of the molecular weight of the polymer in solution. In addition, this degradation may play a role in any loss of bond strength observed when PCA adhesives are aged or heated.

Mechanism of PCA Degradation: The Anomalous Repeat Unit Hypothesis

One possible hypothesis for the observed degradation is that PCAs contain some anomalous re-

peat units that are unstable. To test this conjecture, we examined the carbon nuclear magnetic resonance (^{13}C NMR) spectra of anionic PMECA before and after incubation (Fig. 6).

SEC measurements demonstrated that the presence of acetic acid prevented a significant change in the molecular weight on the timescale of the NMR experiment for the initial sample, but the sample incubated in pure acetonitrile- d_3 had decreased drastically in molecular weight. Nevertheless, there were no significant unassigned signals in either spectrum. The structures of the

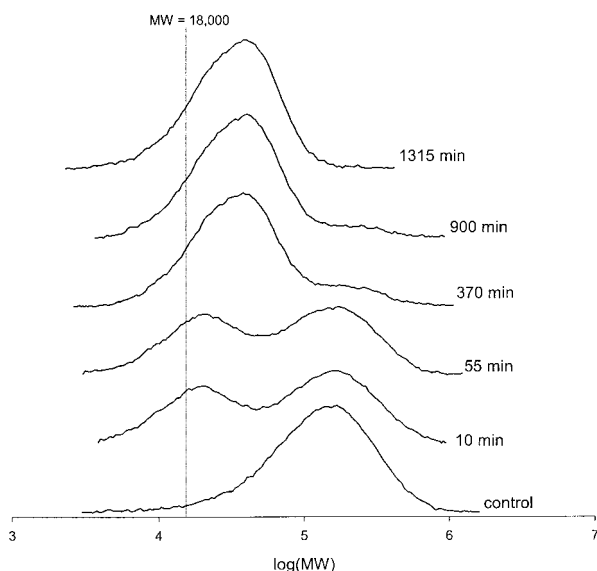


Figure 3. Degradation of triethylamine-initiated PECA in an acetonitrile solution. SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The polymer was dissolved in acetonitrile at a concentration of approximately 1%, held at room temperature, and sampled periodically by SEC. The control sample was dissolved in the eluent, whose acidic character completely inhibited the degradation on the timescale of the experiment. The vertical dotted line was drawn at $\log(M_r) = 4.25$ as a guide to the eye.

initial and degraded polymer were indistinguishable and seem to have contained only the simple, expected repeat unit. If unusual repeat units had been present at a concentration high enough to cause the observed large molecular weight decrease, they should have been detectable by ^{13}C NMR.

In addition, if random scission had occurred along the polymer chain, there should have been a gradual decrease of the molecular weight with the appearance of intermediate sized molecules, contrary to the observed behavior. Therefore, this initial hypothesis is untenable.

Clues to the Mechanism

Three important clues to the mechanism were gleaned from a 1986 paper by Birkinshaw and Pepper,¹⁸ who, with a battery of techniques, examined the degradation of solid samples of PBCA at temperatures above 150 °C:

1. Pyrolysis of the polymer caused it to degrade quantitatively back to its monomer

in accord with the low ceiling temperatures known for PCAs.

2. The molecular weight of samples that had been degraded thermally in an open pan to half their initial mass was essentially unchanged.
3. Samples made with weak bases as initiators or post-treated with strong acid exhibited the best stability in the solid state.

Birkinshaw and Pepper concluded that the mechanism of degradation was unzipping, with a kinetic chain length equal to the degree of polymerization. They also postulated that the unzipping was a free-radical process initiated at the chain origin (i.e., at residue of the polymerization initiator).

Our observations and those of Ryan and McCann¹ are consistent with the former statement

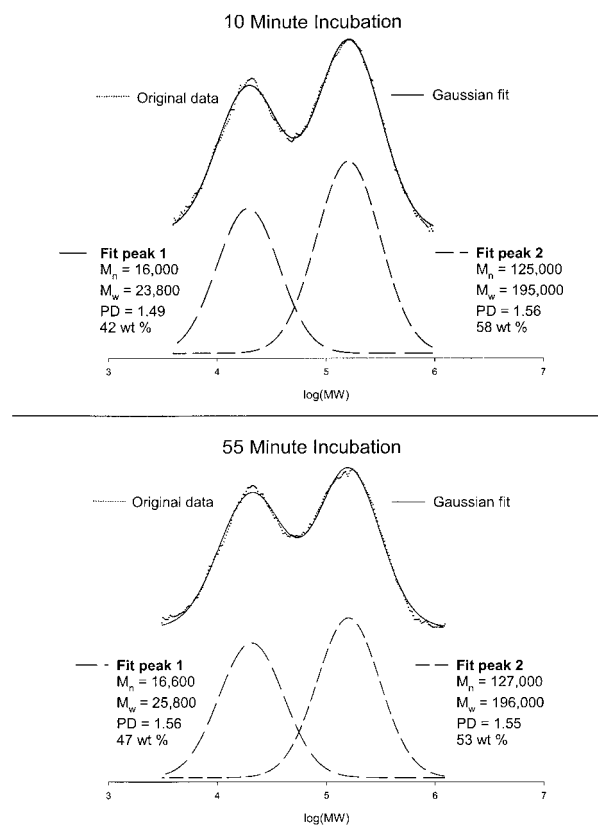


Figure 4. Deconvolution of SEC data for partially degraded PECA. The original SEC data were fitted to the sum of two Gaussian functions by nonlinear regression. By using the coefficients of the fit, two individual peak curves were constructed for each data set, and their individual molecular weight averages were computed.

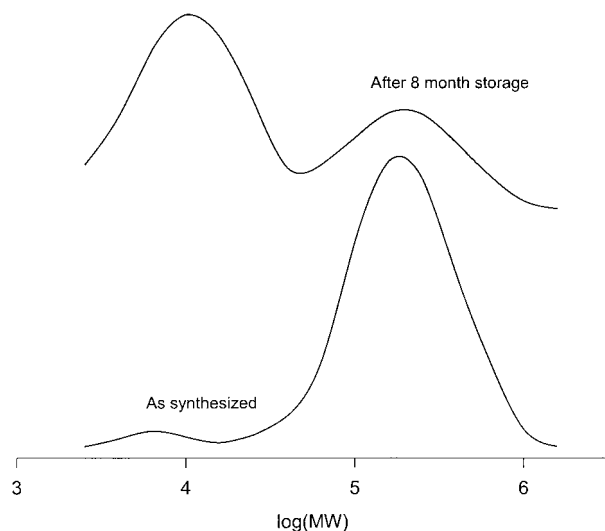


Figure 5. Degradation of triethylamine-initiated PMECA in the solid state. SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The polymer was stored for 8 months at room temperature as a dry powder in a closed bottle between the two measurements.

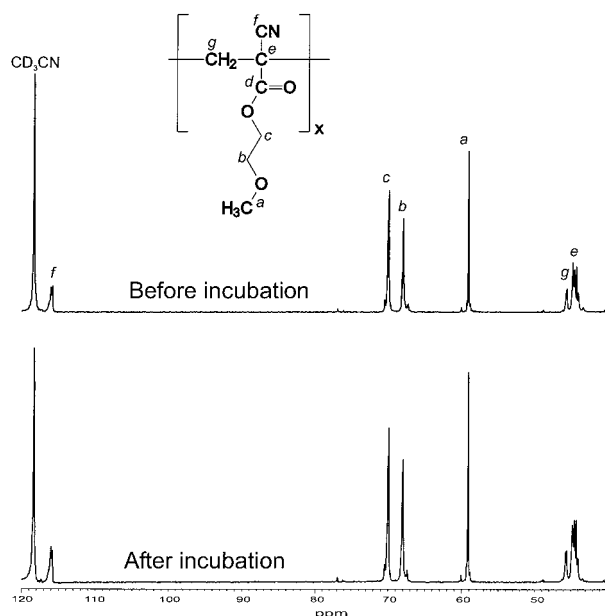


Figure 6. ^{13}C NMR spectra of triethylamine-initiated PMECA. ^{13}C NMR spectra were taken at 75.4 MHz. The initial sample was examined at a concentration of approximately 10 wt % in 90/10 $\text{CD}_3\text{CN}/\text{CD}_3\text{CO}_2\text{D}$. The second sample was incubated for 48 h at 50 °C at a concentration of 10 wt % in CD_3CN and then cooled to room temperature before the spectrum was recorded.

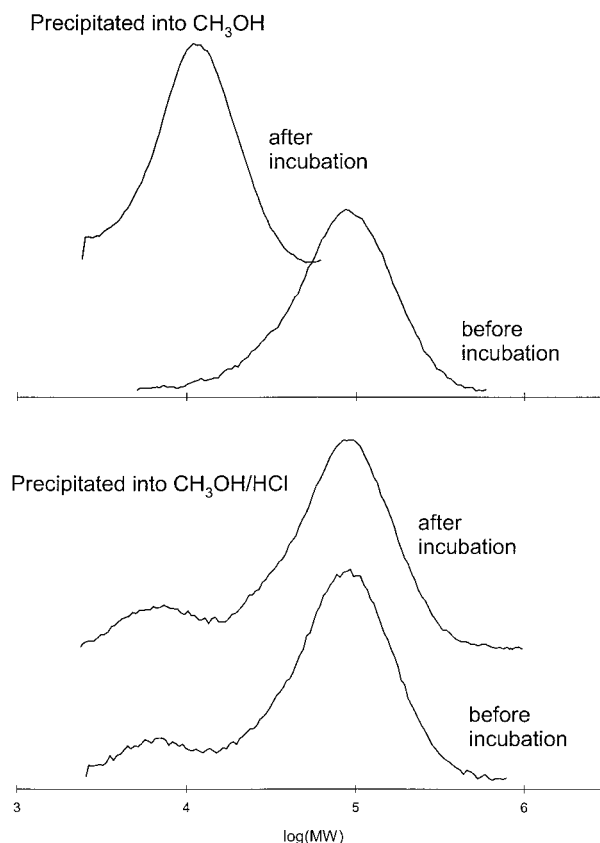


Figure 7. Degradation of triethylamine-initiated PECA in solution. SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. Samples were incubated for 3 days at 50 °C in an acetonitrile solution (approximately 10%).

but not the latter. For example, Ryan and McCann¹ reported that a PCA end-capped with chloride did not degrade. Similarly, we noted that degradation was inhibited by acids. For example, Figure 7 shows molecular weight distributions for two samples of PECA made by anionic polymerization by using triethylamine as the initiator in an ethyl acetate solution and precipitated into excess methanol. The difference is that for the sample in the lower set of curves, a small amount (1% v/v) of concentrated hydrochloric acid was added to the methanol. As can be seen in the figure, the sample precipitated into ordinary methanol degraded completely, but the sample precipitated into acidified methanol was stable when incubated in acetonitrile.

Tacticity Measurements

Further clues to the degradation mechanism were obtained from examination of the tacticity finger-

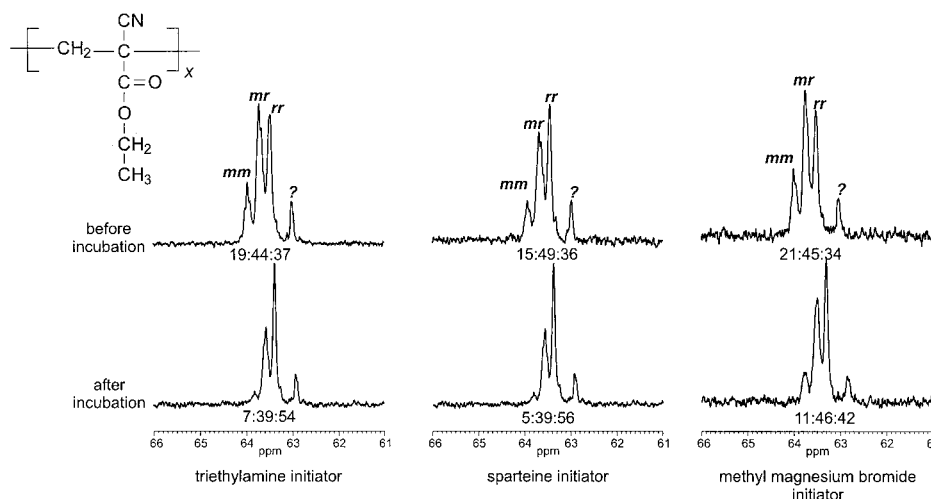


Figure 8. ^{13}C NMR of PECA made with various initiators. ^{13}C NMR spectra in acetone- d_6 were taken at 75.4 MHz. Polymerizations were carried out in THF at room temperature with small amounts of the initiators indicated. Samples were incubated 24 h at 50 $^\circ\text{C}$ in acetonitrile, then concentrated and dried *in vacuo* before reanalysis. The numbers below each spectrum indicate the relative area percentages. The peak marked ? does not appear in all samples of PCA and currently is unassigned.

print of PECA as observed by ^{13}C NMR. The use of different initiators for anionic polymerization led to slightly different distributions of stereoisomers. For example, Figure 8 shows close-ups of the CH_2O signals for samples of PECA initiated with triethylamine, sparteine, and methyl magnesium iodide before and after incubation in an acetonitrile solution. The three main peaks in Figure 8 are labeled with triad tacticity notations drawn from our recent study¹⁹ that are contrary to previous literature.^{20–21}

That all three samples changed in the same way and converged to similar distributions of stereoisomers was an indication that they all were experiencing the same equilibration reaction. Apparently, PECA became increasingly syndiotactic as it equilibrated under these conditions. The observed tacticity changes were not consistent with some kind of chain scission mechanism, where changes would be expected to be negligible.

The small upfield peak (labeled ? in the Fig. 8) is a mystery. It occurred in most but not all samples of the PCAs we studied. The intensity and position of this peak did not change after incubation. Distortionless Enhancement Polarization Transfer (DEPT) spectra indicated that this peak was due to a CH_2 group. Perhaps it was caused by end-groups on the polymer chains, but we lack sufficient evidence to make an assignment. Further work is required to ascertain whether there

is any connection between this peak and the degradation behavior of the polymers.

Mechanism of PCA Degradation: Chain-End Equilibration.

The chain end of a PCA from anionic polymerization is a stabilized carbanion that is in equilibrium with the monomer. The chain end can be protonated by water, methanol, or some acid to form a dormant species (Fig. 9). However, this dormant chain end is acidic because of the two electron-withdrawing groups adjacent to the $\text{C}-\text{H}$. Adventitious bases, (especially bases left unreacted from polymerization, or possibly basic impurities in the solvent), deprotonate the dormant polymer, and the chain then reenters the equilibrium. The addition of acid inhibits the dep-

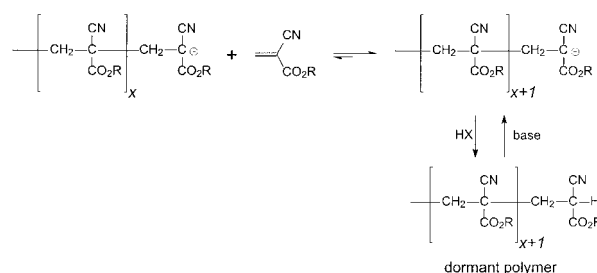


Figure 9. Mechanism of chain degradation for PCAs.

rotation at the chain terminus and prevents the molecule from entering the equilibrium. No plausible mechanism can be conceived for acid inhibition of degradation at the chain origin, nor should the presence of acetic acid affect free-radical processes.

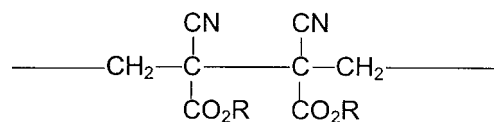
The freed monomer should be capable of reacting with any nucleophiles that it finds. This process eventually builds new (daughter) chains that are responsible for the low molecular weight fraction observed by SEC. The low molecular weight peak in Figure 3 shows a gradual increase in molecular weight (compare with the reference line drawn at $M_w = 18,000$), yet the high molecular weight fraction was diminishing in intensity without a significant shift of position. These observations were consistent with the chain growth from the addition of new monomer released from the high molecular weight material, and exactly the same observations were made by Ryan and McCann.¹

Another significant point is that the anionic polymerization of cyanoacrylate (CA) monomers is known to be very fast, but the ceiling temperature of the resulting polymers is rather low. This means that the reverse reaction (i.e., chain unzipping) also must be rather fast. We agree with the conclusions of Ryan and McCann¹ that the monomer and polymer are in equilibrium, apparently with significant concentrations of the monomer present, even at room temperature.

Our observations are in accord with the mechanism proposed by Ryan and McCann¹ and are summarized as follow:

1. The CA monomer and polymer are in rapid, dynamic equilibrium.
2. During synthesis, the concentration of the monomer is very high, a condition that favors the production of long chains.
3. The anionic end-group is protonated by water or other acids at the end of the polymerization reaction, forming a dormant species.
4. Base deprotonates this dormant chain end, reactivating the polymerization equilibrium.
5. The monomer that is released during the equilibrium adds rapidly to any nucleophiles present, forming new chains.
6. Because the concentration of the monomer in the new equilibrium is much lower than that during polymerization, the new chains

• Termination by coupling:



• Termination by disproportionation:

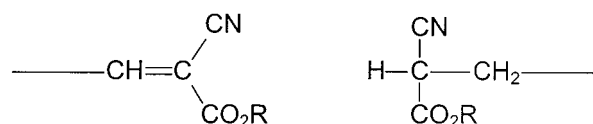


Figure 10. End-groups from free-radical polymerization of PCAs.

that form have drastically lower molecular weights.

7. Acid inhibits the deprotonation of the chain ends, preventing the equilibration.

DEGRADATION OF FREE-RADICAL PCAS

Termination Modes and Degradation Mechanisms

For free-radical polymerization, the two different modes of termination give rise to three different end-groups (Fig. 10). The relative amounts of termination by coupling versus disproportionation for PCAs is not known; however, for other acrylic polymers such as poly(methyl methacrylate) (PMMA), disproportionation predominates.²²⁻²³ One might anticipate that all three of the possible end-groups may be present in the radically initiated PCAs. Note that the structure at the lower right in the figure is identical to that produced by protonation of the chain end from anionic polymerization. If our proposed mechanism was correct, PCA chains with this end-group should have exhibited the same instability as those made by anionic polymerization, whereas chains possessing either of the two other end-groups should not have degraded in molecular weight under the identical conditions. This was precisely what was observed for a sample polymerized using a free-radical initiator (Fig. 11). Some of the sample degraded, and the rest remained unchanged under conditions that led to complete degradation of the nucleophile-initiated PCA.

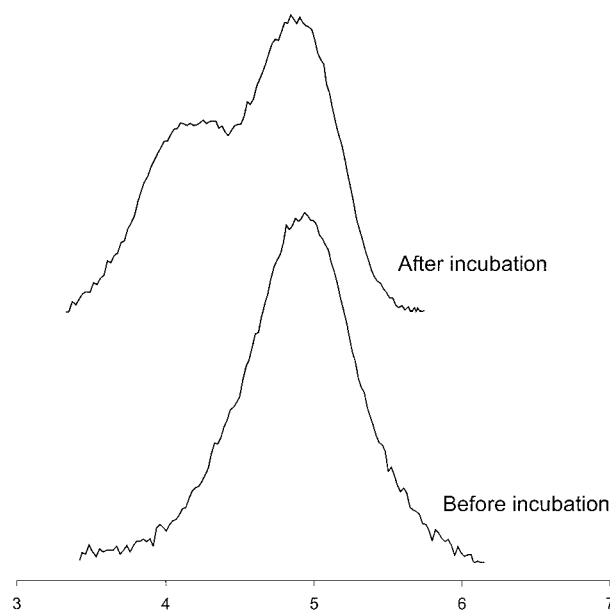


Figure 11. Degradation of radical-initiated PECA in an acetonitrile solution. SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The incubated polymer was dissolved in acetonitrile at a concentration of approximately 10%, held at 50 °C for 24 h, and then isolated by drying *in vacuo*.

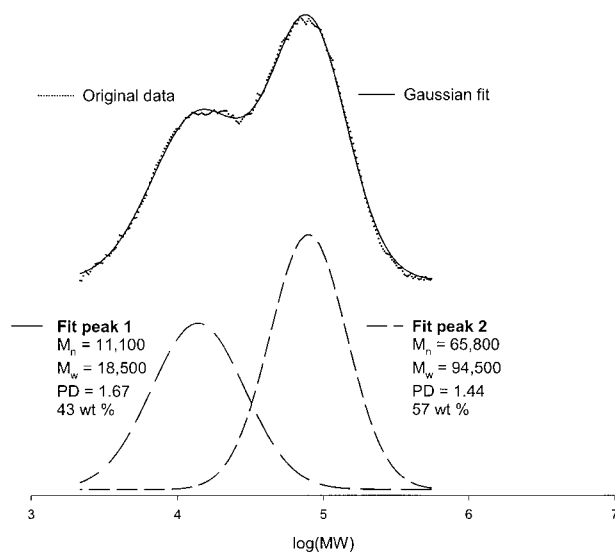


Figure 12. Deconvolution of SEC data for partially degraded PECA. SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The incubated polymer was dissolved in acetonitrile at a concentration of approximately 10%, held at 50 °C for 24 h, and then isolated by drying *in vacuo*.

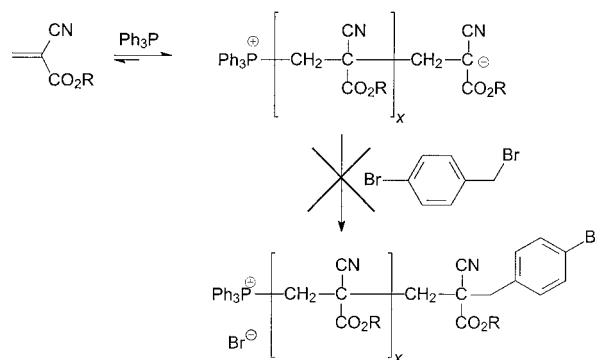


Figure 13. Attempted end-capping of nucleophile-initiated PCA.

As before, we were able to deconvolute the bimodal SEC curve of the partially degraded polymer into two contributing peaks (Fig. 12).

According to this hypothesis, the data in Figure 11 are consistent with approximately 80% of the chain termination reactions for this sample occurring by disproportionation and with the remaining 20% by combination. The relative proportions were not very different than those observed for the free-radical polymerization methyl methacrylate (MMA).^{22–23}

It was clear that, although radical polymerization decreased the severity of the degradation of the PCAs, by itself it did not stop degradation completely.

STABILIZATION OF PCAS

Attempted End-Capping

If chain degradation occurs through unzipping from the terminus, then it should be possible to stop the process by end-capping the chains with a suitable reagent. This technique is used commercially to stabilize polyoxymethylene, a polymer with a low ceiling temperature. For example, Ryan and McCann¹ mentioned without details the possibility of producing PCAs with chloride end-groups. We attempted an analogous procedure using 4-bromobenzyl bromide (Fig. 13) to end-cap nucleophile-initiated PBCA, but the reaction failed to proceed according to our expectations. No trace of the aromatic end-group could be detected by proton nuclear magnetic resonance (¹H NMR).

Presumably, other, more reactive reagents might work in this scheme, but we did not pursue

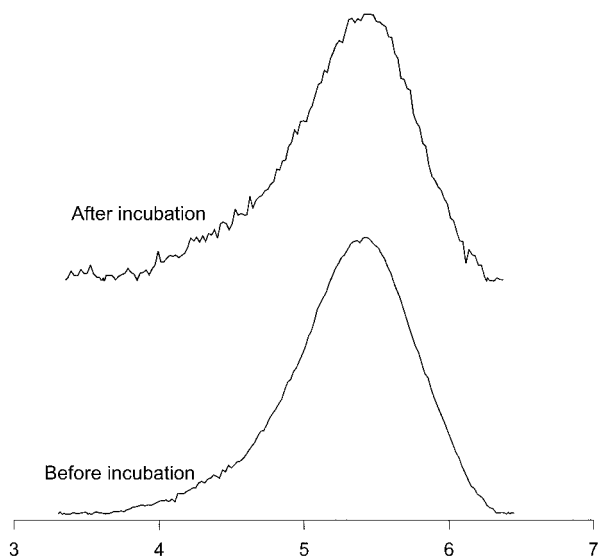


Figure 14. SEC of the stable copolymer of ECA and MA (70/30). SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The incubated polymer was dissolved in acetonitrile at a concentration of approximately 10%, held at 50 °C for 48 h, and then isolated by drying *in vacuo*.

these variations because we found a simple, alternative method for stabilizing PCAs.

Copolymerization

Another common technique for stabilizing polymers against unzipping is to incorporate a small amount of a second, more stable monomer into the chains. For example, commercial PMMA usually is copolymerized with a little methyl acrylate, and polyoxymethylene can be copolymerized with some ethylene oxide. The ceiling temperature of the additive monomer is much higher than that of the main monomer, so that the unzipping stops when the second monomer is at the chain end. Following this concept, we attempted to prepare copolymers of cyanoacrylates with minor amounts of ordinary monomers such as MMA, methacrylic acid (MA), and the like. Unlike our attempts at end-capping, this stabilization technique worked very well.

Because acids are successful in preventing the decomposition reaction of PCAs, we first prepared copolymers of cyanoacrylates with MA. Naturally, anionic polymerization of MA is impossible, so we used conventional free-radical polymerization conditions. These copolymers were found to be stable. For example, a sample prepared by free-

radical polymerization from a monomer feed of 70% ECA and 30% MA exhibited no degradation under conditions where nucleophile-initiated PECA degraded completely (Fig. 14). We later discovered that neutral comonomers were equally capable of stabilizing PCAs. Even as little as 5% of MMA as the comonomer was sufficient to stop the degradation completely (Fig. 15).

Note that it is convenient to carry out free-radical copolymerizations of cyanoacrylates with neutral monomers in the presence of acetic acid to prevent unwanted anionic polymerization.

The reactivity ratios of dissimilar monomers such as cyanoacrylates and MA might lead to problems in incorporation. Therefore, we examined samples of 2-methoxyethyl cyanoacrylate (MECA)-*co*-MA (70/30 wt) and MECA-*co*-MA (90/10 wt) by high-performance liquid chromatography (HPLC) to determine compositional variations. These measurements found only an insignificant trace of PMECA homopolymer in the copolymer. We do not know whether this material was formed in the radical polymerization or was present in the monomer before reaction. Nevertheless, the incorporation of MA into the copolymers seems to have occurred without difficulty.

Unfortunately, simple acrylic monomers cannot be incorporated statistically into copolymers with cyanoacrylates by anionic polymerization. The stabilizing effect of two electron-withdrawing

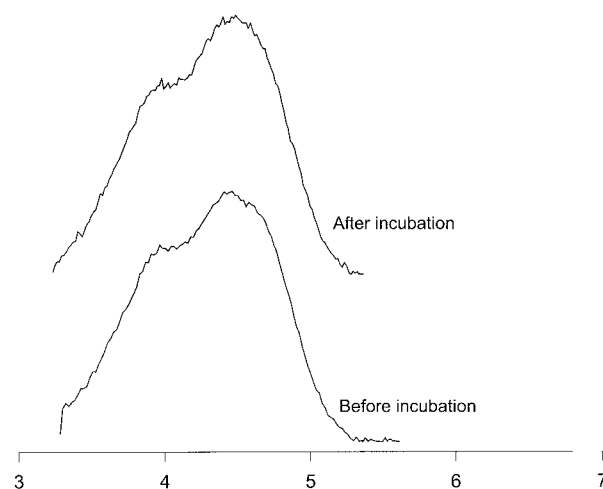


Figure 15. SEC of the stable copolymer of ECA and MMA (95/5). SEC was measured by using 20/80 dichloroacetic acid/dichloromethane eluent and polystyrene calibration. The incubated polymer was dissolved in acetonitrile at a concentration of approximately 10%, held at 50 °C for 6 h, and then isolated by drying *in vacuo*.

groups on the cyanoacrylate repeat unit is so strong that crossover to a less stabilizing monomer does not occur. This situation is unfortunate because molecular weight stabilization of PCA adhesives would have tremendous practical value.

Free-radical copolymerization is a serviceable technique for the preparation of stable PCAs. Because the polymers can be stabilized with very small amounts of comonomer, the physical properties of the material should not be changed significantly.

CONCLUSIONS

We found that PCAs are inherently unstable, and, when possible, equilibrate with their monomer, in agreement with the observations of Ryan and McCann.¹ This process leads to severe degradation of the molecular weight of the polymer by an order of magnitude or more. Adventitious base is sufficient to promote the degradation. The mechanism of degradation appears to involve base-catalyzed unzipping from the chain terminus, followed by re-equilibration of the chains. The degradation is inhibited by acids. Free-radical copolymerization with appropriate monomers provides perfectly stable polymers.

This degradation mechanism may play a role in the decrease of adhesive bond strength observed on heating¹⁵ and also contribute to the reputed poor resistance of PCA adhesives to prolonged contact with water.

EXPERIMENTAL

Cyanoacrylate monomers were obtained from the Henkel Adhesives Corporation (Elsin, IL) and were used without further purification. Methyl magnesium iodide solution (3.0 M in diethyl ether) was obtained from Aldrich (Milwaukee, WI). SEC was carried out using three PL gel 10- μ m mixed-bed columns calibrated with narrow molecular weight distribution polystyrene standards. The eluent was dichloromethane/dichloroacetic acid (DCM/DCAA) (20/80%) containing 0.01 M of tetrabutyl ammonium acetate. HPLC separations of copolymers were performed on a LiChrospher Si100 10- μ m silica 4.6 $\times$ 250 mm column. The eluents were "Solvent A" (95/5 tetrahydrofuran/acetic acid) and toluene. Linear gradient elution was performed at 1.0 mL/min from 60%

Solvent A in toluene to pure Solvent A over 10 min with a final hold for 10 min at 100% Solvent A. Detection was done with an evaporative light scattering detector set at 80 °C and 20 psi nitrogen (this detector provided a signal for all solutes of lower volatility than the mobile phase solvents). The acetonitrile used for the incubation studies was HPLC grade with a nominal water content of less than 0.005%.

Synthesis of PMECA with Triethylamine as the Initiator

To a stirred solution of 200 g of MECA in 800 g of ethyl acetate at 25 °C under argon was added 8 μ L of triethylamine. The resulting mixture was stirred at 25 °C for 16 h and diluted with an additional 800 g of ethyl acetate, and the reaction mixture was poured into excess methanol. The precipitated polymer was filtered and dried, producing 132 g (61%) of a white, fibrous solid.

SEC in DCM/DCAA immediately after isolation: M_n = 76,700; M_w = 233,000; polydispersity (PD) = 3.04.

Synthesis of PECA with Methyl Magnesium Iodide as the Initiator

To a stirred solution of 2.24 g of ECA in 50 mL of tetrahydrofuran at 25 °C under nitrogen was added 30 μ L of a 3.0 M solution of methyl magnesium iodide in diethyl ether. The resulting mixture was stirred at 25 °C for 15 min under nitrogen. The reaction mixture was poured into excess methanol. The precipitated polymer was filtered and dried, producing 0.89 g of a white, fibrous solid.

Synthesis of PECA with AIBN as the Initiator

To a stirred solution of 3.0 g of ECA in 10 mL of 90/10 (v/v) of ethyl acetate/acetic acid was added 25 mg of AIBN. The resulting mixture was deaerated by sparging with nitrogen for 10 min, then heated at 50 °C for 21 h in a constant temperature bath. The reaction mixture was slowly poured into excess methanol. The precipitated polymer was filtered and dried, producing 0.53 g of a white, fibrous solid.

Synthesis of PBCA with Triphenyl Phosphine as the Initiator and Attempted End-Capping

A stirred solution of 5.0 g (33 mmol) of *n*-butyl cyanoacrylate in 50 mL of THF was cooled to -78

°C under nitrogen and treated with a solution of 0.050 g (0.19 mmol) of triphenyl phosphine in the same solvent. The reaction mixture gelled immediately but gradually became fluid as it was warmed to room temperature. A solution of 0.15 g (0.60 mmol) of 4-bromobenzyl bromide in 1 mL of THF was added, and the mixture was stirred at room temperature overnight. The reaction mixture was poured into excess methanol to precipitate the polymer. After drying, 2.0 g (40%) of a white powder was obtained. Examination of the polymer by ¹H NMR showed no trace of aromatic protons, even at a greatly expanded ordinate, indicating that the end-capping reaction had failed.

Synthesis of 95% ECA/5% MMA Copolymer with AIBN as the Initiator

A 125-mL heavy-walled bottle was rinsed with 5% HCl and then dried at 150 °C for 2 h. A stream of nitrogen was run into the bottle while it was cooling and throughout the addition of reagents. 0.5 g of MMA was added to the bottle, followed by 10 g of ethyl acetate and 0.030 g of AIBN. The AIBN was allowed to dissolve and was followed by the addition of 9.5 g of ECA. The bottle was sealed with a Teflon seal and an aluminum cap, then tumbled at 60 °C in a constant temperature bath for 16 h. The resulting polymer was diluted with ethyl acetate/methanol (75/25 volume) and precipitated into water. The polymer was collected by filtration and dried *in vacuo*.

Synthesis of 70% ECA/30% MA Copolymer with AIBN as the Initiator

A 2-L three-necked round-bottom flask was acid rinsed, dried for 2 h at 150 °C, and blanketed with nitrogen while cooling and throughout the addition of reagents. The following reagents were added: 51 g of MA, 680 g of chlorobenzene, 0.51 g of AIBN, and 119 g of ECA. The flask was fitted with an overhead stirrer and a condenser topped with a nitrogen bubbler. The flask was put in a constant temperature bath at 60 °C and stirred for 15 h. The resulting polymer solution was diluted with chlorobenzene and precipitated into excess heptane. The polymer was dried *in vacuo* for 24 h, dissolved in an acetone/methanol mixture, and then reprecipitated into water. The final product was dried *in vacuo* for 24 h.

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