Copolymerization of Acrylic Acid with 1-Substituted Imidazoles

D. H. Davies,* J. D. B. Smith, and D. C. Phillips

Insulation and Applied Chemical Research, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania. *Received July 12, 1972*

ABSTRACT: The photoinitiated (254-nm) and the electroinitiated (100 mA, 25–75 V) bulk copolymerization of acrylic acid (AA) with 1-substituted imidazoles is described. Both initiation techniques produced low polymer yields from 2-methyl-1-vinylimidazoles (2-MVI) and 1-vinylimidazole (VI), with somewhat higher yields obtained from 1-methylimidazole (MI). The electroinitiated copolymerization gave more product in each case, but both initiation methods showed a relative rate sequence of MI > 2-MVI > VI. The rate of copolymerization was dependent on the intensity of the ultraviolet light and on the electrolytic current density. There was a small but observable thermal reaction in which the relative rate sequence was the reverse of that above. The copolymer composition was essentially invariant between the methods of initiation and substituted imidazole with an approximate 3:1 mole ratio of AA to alkylimidazole being found. Addition of *p*-methoxyphenol lowered the reaction rate. Formation of an activated imidazolium acrylate complex is postulated to explain the results. The product yield is thought to be determined by the equilibrium concentration of the complex and hence by the basicity of the imidazole and by the intensity of the initiating process. The copolymer composition is established by the relative reactivity of the imidazolium acrylate radical to acrylic acid and is therefore moderately independent of the imidazole substituent.

Significant kinetic and product composition correlations have been found between electroinitiation and shortwave ultraviolet photoinitiation in the zinc salt catalyzed copolymerization of styrene and diethyl fumarate.[1] In this system, the results can be explained by the rate-determining formation of a charge-transfer complex between the styrene and a diethyl fumarate metal–salt complex. The system bears a strong resemblance to the donor–acceptor model by Gaylord,[2] which has been found to apply to both metal-catalyzed and uncatalyzed systems. The uncatalyzed systems depend on the existence of enough charge separation in the complex, without the increased electron deficiency in the acceptor that results from the metal–salt complex.[3]

It seemed likely that photo- and electroinitiation correlations would be found where latent donor–acceptor tendencies exist and can be strengthened by the initiating process. This work is an attempt to extend the correlation into systems where there is sufficient charge separation to avoid the need for a metal–salt accelerator.

Comparatively little work has been done on the polymerization of alkylvinylimidazoles. Murahashi[4] reported the photoinitiated polymerization of some alkylvinylimidazoles and their copolymerization with styrene and methyl methacrylate. Tazuke *et al.*[5] found that oxidizing metal salts would catalyze the photopolymerization of 2-alkyl-1-vinylimidazoles and postulated, from spectroscopic and kinetic data, that the polymerization proceeded through photoabsorption by the complex through the charge-transfer band. This method was favored over the possibility of photoexcitation of the uncomplexed monomer. Nonoxidizing metal salts such as zinc acetate were less effective. Other investigations[6] showed that oxidizing metal salts could serve as electropolymerization catalysts in imidazole homopolymerization. This indicated that these monomers, normally difficult to polymerize, might be worth further study from the point of view of comparison between initiation systems. Further, the analysis could possibly distinguish between the photoinitiation alternatives discussed by Tazuke, since the existence of strong kinetic correlations between the initiation methods can eliminate some possible mechanistic routes.[1]

The copolymerization of substituted imidazoles with acrylic acid offers interesting possibilities, since there is considerable evidence for imidazolium ion formation and subsequent polymerization in acids.[7] The acrylic anion–imidazolium cation complex could then provide a suitable charge separation to induce a copolymerization based on the complex. Overberger *et al.*[8] reported a 55% conversion using acrylic acid and 4(5)-vinylimidazole in a reaction initiated with azobis(isobutyronitrile) (AIBN) at 70°. The copolymerization has also been reported in the patent literature, but without significant characterization.[9,10]

The present communication describes the photo- and electroinitiation of acrylic acid (AA) with 1-vinylimidazole (VI), 2-methyl-1-vinylimidazole (2-MVI), and 1-methylimidazole (MI).

Experimental Section

Acrylic acid monomer (Eastman Kodak) was purified by distillation under reduced pressure and stored at 0° under nitrogen. Inhibitor (*p*-methoxyphenol, Eastman Kodak) was purified by recrystallization from diethyl ether. 2-Methyl-1-vinylimidazole, 1-vinylimidazole (BASF), and 1-methylimidazole (Aldrich Chemical) were purified by distillation under reduced pressure.

Electroinitiated polymerizations were conducted at 0° in a 500-ml reaction flask equipped with a stirrer and a nitrogen inlet–outlet. The electrolytic cell contained two identical platinum electrodes (2.0 × 5.0 cm) separated by 4.0 cm. Polymerizations were carried out under conditions of constant current (100 mA) using a dc power supply (Northeast Scientific 0-360 V, 0-230 mA).

Samples were photopolymerized by irradiation with 254-nm light from a PQX uv lamp (UV Products Inc.). Fused silica sample tubes (1-cm diameter) with good 254-nm transmittance were used and a range of intensities utilized by placing these sample tubes at various distances from the light source. The lamp pro-

(1) D. H. Davies, D. C. Phillips, and J. D. B. Smith, *J. Poly. Sci., Part A-1*, 10, 3253 (1972).
(2) N. G. Gaylord and A. Takahashi in "Addition and Condensation Polymerization Processes," N. A. Platzer, Ed., Washington, D. C., American Chemical Society, 1969.
(3) H. Gilbert *et al.*, *J. Amer. Chem. Soc.*, 78, 1669 (1956); and ref 2, p 100.
(4) S. Murahashi, S. Nozakura, A. Umehara, and K. Obala, *Kobunshi Kagaku*, 21, 625 (1964).
(5) S. Tazuke and S. Okamura, *J. Poly. Sci., Part A-1*, 7, 851 (1969).
(6) D. C. Phillips, J. D. B. Smith, and D. H. Davies, *Electrochem. Soc., Extended Abstr.* 72-1, 248 (1972).
(7) J. C. Salamone, B. Snider, S. C. Israel, P. Taylor, and D. Raia, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, 13, No. 1, 271 (1972).
(8) G. C. Overberger, J. C. Salamone, I. Cho, and H. Maki, *Ann N. Y. Acad. Sci.*, 155, 431 (1969).
(9) H. Spoor, H. Pohlemann, G. Florus, and F. Schander, French Patent 1,477,147 (1967).
(10) N. Mori, Y. Asano, and H. Kimura, Japanese Patent 69 07,395 (1969).

Table I
Product Characteristics—Acrylic Acid:Imidazole Copolymerization

Imidazole	Initiation System[b]	Copolymer Content by Elemental Anal. AA:Imidazole	% Conversion after 30 hr	Intrinsic Viscosity 0.10 *N* HCl 38° (dl g^{-1})
1-Methyl	Photo-[a]	0.73:0.27 (a)	7	0.41
	Electro-	0.75:0.25 (b)	13	0.28
2-Methyl-1-vinyl	Photo-	0.75:0.25 (c)	1.2	
	Electro-	0.80:0.20 (d)	8	4.6
1-Vinyl	Photo-	0.77:0.23 (e)	0.2	
	Electro-	0.75:0.25 (f)	3	4.9

Copolymer Reaction	Calcd (%)			Found (%)		
	C	H	N	C	H	N
a	52.5	6.0	10.1	52.4	6.9	10.3
b	52.5	6.1	9.4	49.5	6.2	9.5
c	52.3	6.0	9.4	52.2	5.9	10.1
d	51.7	5.9	7.6	48.1	6.0	7.8
e	51.9	5.6	8.0	49.5	5.9	8.1
f	54.0	5.8	9.0	48.8	6.1	9.1

[a] This product showed considerable variation, analysis shown applied only to below 30-hr photoexposure. [b] Photoinitiation, 31,500 μW/cm^2, 254-nm light. Electroinitiation, 100 mA/25–75 V.

duces 254-nm radiation almost exclusively and intensities up to 32,000 μW/cm^2. Continuous air cooling maintained a 25° ambient temperature, and the sample preparation and polymerization were done under N_2.

Products were isolated by dilution with excess absolute methanol. The 2-MVI-AA, and the VI-AA copolymers were purified by dissolving in 0.2 *N* HCl and precipitating into absolute methanol. The product yield determinations were obtained gravimetrically after washing the product with excess absolute methanol, followed by purification as above, and drying overnight in a vacuum oven at 40°. The MI-AA copolymer was dissolved in water and reprecipitated from methanol. The precipitate was squeezed between filter paper to remove solvent and dried under vacuum at room temperature to avoid the possibility of further reaction.

The copolymers were characterized by ir spectroscopy (KBr pressed disk) and elemental analysis. Intrinsic viscosities were measured in 0.1 *N* HCl at 38° using a standard Ostwald viscometer. Nuclear magnetic resonance spectra (60 MHz) were obtained on a Varian A-60 instrument, utilizing D_2O solutions of the sample. The acid exchange peak at δ 4.6 was used as internal reference.

Ultraviolet intensities were measured using an RCA 935 (S5) photocell fitted with a G-571-2537 calibrated interference filter (254 nm with 25-nm bandwidth) supplied by Oriel Optics Inc., Stanford, Conn. Confirmatory readings were taken using a J225 solid-state sensor calibrated for 254-nm radiation (UV Products Inc., San Gabriel, Calif).

Results and Discussion

Irradiation of 1:1 mole ratio mixtures of both AA:2MVI and AA:VI resulted in products that formed a light, gelatinous precipitate on dilution with excess methanol. Prior to addition of the methanol, the bulk mixture remained homogeneous and intensified in color somewhat. The resulting product was insoluble in water as well as in a wide variety of protic and aprotic solvents, and showed hydrogel properties similar to the properties of radical initiated homopolymers of the imidazoles.[7] The ir spectra clearly showed the presence of both carbonyl and imidazole absorption bands and elemental analysis produced the results shown in Table I. An approximate 3:1 mole ratio of AA:imidazole was found for both systems. The copolymerization was slow in both instances, but with the 2-MVI being more rapid than the VI. Addition of *p*-

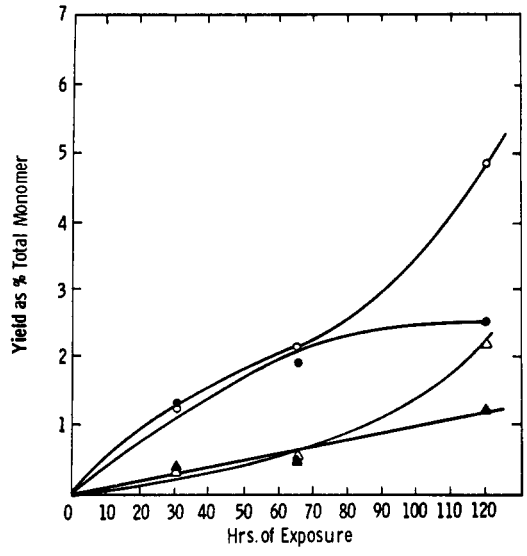


Figure 1. Photoinitiation, copolymer yield *vs.* exposure time. (▲) VI-AA, 100 ppm of inhibitor; (△) VI-AA, no inhibitor; (●) 2-MVI-AA, 100 ppm of inhibitor; (○) 2-MVI-AA, no inhibitor. Irradiation with 31,500 μW/cm^2 254 nm.

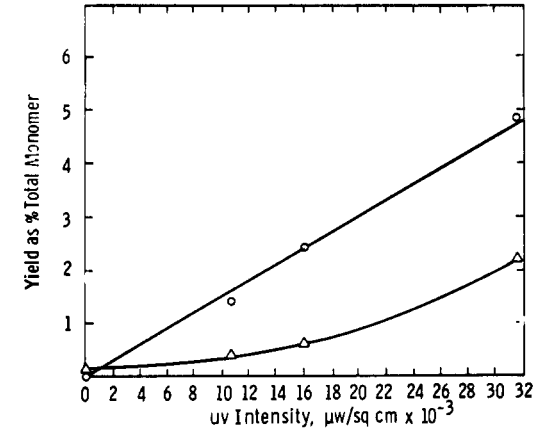


Figure 2. Photoinitiation, copolymer yield versus uv intensity. Irradiation with 254 nm. (△) VI-AA, no inhibitor; (○) 2-MVI-AA, no inhibitor; both at 120-hr irradiation.

methoxyphenol (100 ppm) slowed the reaction significantly only after 60-hr exposure. The results for both monomer systems are given in Figure 1 for irradiation with 31,500 μW/cm^2 of 254 nm. Both monomer systems showed a positive rate dependence on uv intensity, as shown in Figure 2. The 2-MVI-AA system showed good first-order dependency with respect to the initiation intensity, with the VI-AA having a higher order dependency. These order dependency plots shown in Figure 3 represent reaction after 120-hr irradiation.

Control experiments, where 1:1 mole ratios of both monomer mixtures were kept in the dark for 120 hr, resulted in a very small (0.2%) yield for the VI-AA system and a barely detectable trace for the 2-MVI-AA system. Irradiation of the imidazoles alone gave no detectable methanol-insoluble product after 120 hr at 31,500 μW/cm^2 of 254-nm uv. Irradiation of the acrylic acid alone gave a rapid gelling of the material within hours. The product, presumably poly(acrylic acid), was sparingly soluble in methanol but, unlike the copolymers, was easily dissolved in water.

Electroinitiation at 100-mA current of a 1:1 mole ratio composition of the two monomers gave the results shown in Figure 4. The 2-MVI-AA system was again significantly

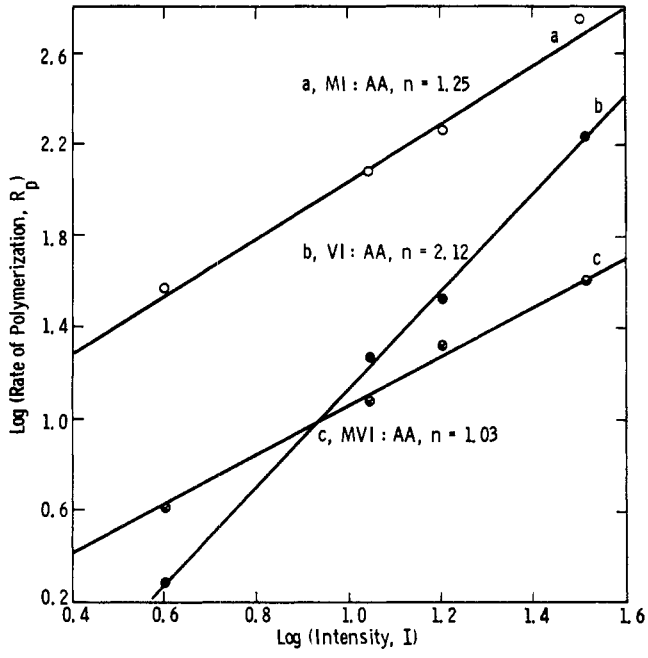


Figure 3. Determination of the intensity exponent, n, in the rate equation (see text).

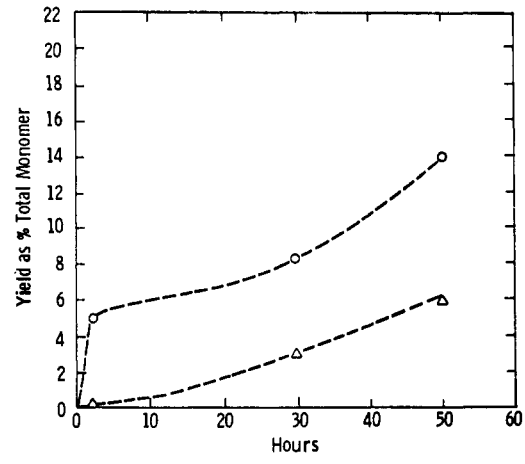


Figure 4. Electroinitiation, copolymer yield *vs.* current duration. (○) 2-MVI-AA, no inhibitor; (△) VI-AA, no inhibitor; both at a current of 100 mA/25-75 V.

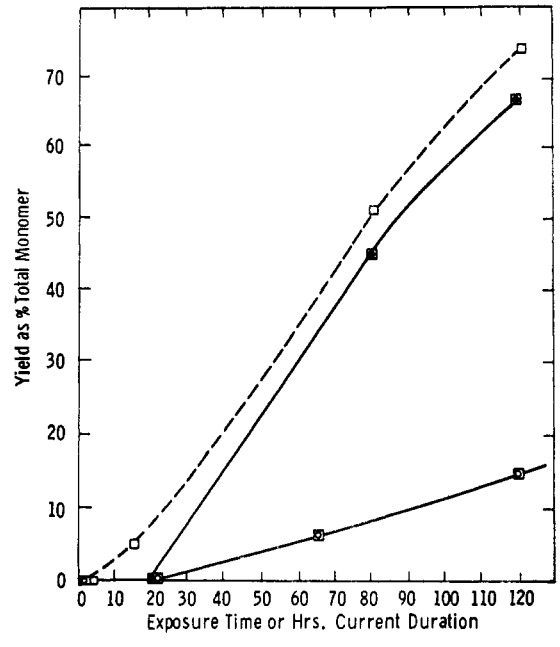


Figure 5. Electro- and photoinitiation; copolymer yield *vs.* current duration and exposure time. (□) MI-AA, no inhibitor, electroinitiated, 100 mA/25-75 V; (▣) MI-AA, no inhibitor, photoinitiated, 10,300 μW/cm^2 254 nm; (▣) MI-AA, no inhibitor, photoinitiated, 31,500 μW/cm^2 254 nm.

more reactive than the VI-AA system. The yields obtained with electroinitiation were higher than with photoinitiation, which is in contrast with the results found with the zinc salt catalyzed styrene-diethyl fumarate system.[1] The extracted copolymers had very similar solubility characteristics to those products obtained by photoinitiation. The elemental analysis results again indicated an approximate 3:1 mole ratio of AA:imidazole (see Table I) and the ir spectra were comparable to the previous samples. The difficulty in accurate control in electropolymerization, together with the low yields, makes meaningful kinetic analysis somewhat difficult; however, the relative rate of copolymerization (τ_{rel} = τ(photo)/τ(electro) at 50-hr polymerization time), obtained from Figures 3 and 5, was 0.14 for 2-MVI-AA. This compares favorably with the equivalent value obtained for VI-AA which was 0.13 (both results for 31,500 μW/cm^3). This result is indicative of the fact that the same initiation step could be operative in both systems.

The results for the copolymerization of 1-methylimidazole and acrylic acid showed some significant deviations from the other two monomer systems described above. The results for photoinitiation (31,500 and 10,300 μW per cm^2) and electroinitiation (100-mA current) of a 1:1 mole ratio mixture of the MI and AA are shown in Figure 5. Much higher product yield was obtained, with the electroinitiated again faster than photoinitiated. An unusual inhibition period up to 20 hr was found with the photoinitiation. After 20 hr, the conversion was a linear function of time for electro and both uv intensity photoinitiations. The τ_{rel} for MI:AA was = 0.85 (50 hr, 31,500 μW/cm^2), which is significantly different from the equivalent value found for 2-MVI:AA and VI:AA.

The product obtained from both electro- and photoinitiation was a tan rubber-like solid which, after purification and drying, was transparent and strongly adherent to glass. The product appeared to react further on drying above 40° to give a hard brittle solid. Unlike the 2-MVI:AA and VI:AA copolymers, after purification, the MI:AA material was somewhat soluble in water. To establish that it was a copolymer, the material was washed successively with water and the ir spectrum examined. No changes occurred, with the imidazole and acrylic acid absorption bands maintaining approximate equivalence. Elemental analysis for the product after 30-hr polymerization time is shown in Table I. Although the above data indicate significant differences between the vinylimidazole and the methylimidazole copolymerizations, there were also some similarities. Electropolymerization gave a copolymer, again exhibiting the approximate 3:1 AA:imidazole composition. Photoproduced copolymer, however, was somewhat variable in composition, with elemental analysis indicating varying amounts of copolymerized acrylic acid, depending on the particular conditions. At the lower percentage conversions, corresponding to 30-hr irradiation at 31,500 μW/cm^2, approximately a 3:1 mole ratio of monomers was found. These data are listed in Table I. Further correlations between the copolymerizations can be seen from an analysis of the effect of uv intensity variation on copolymer per cent conversion of the

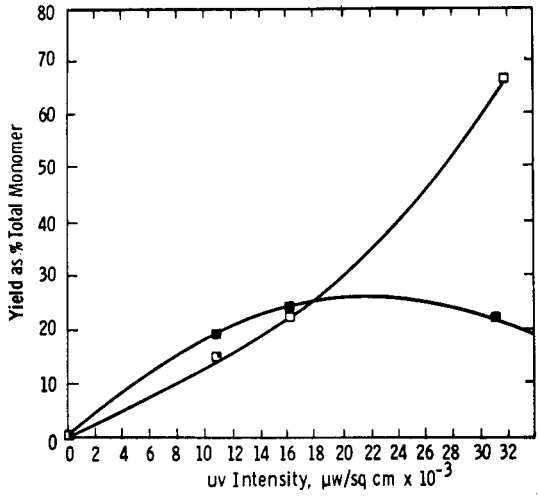
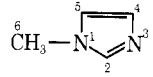


Figure 6. Photoinitiation, copolymer yield *vs.* uv intensity. Irradiation with 254 nm. (□) MI–AA, no inhibitor; (■) MI–AA, 100 ppm of inhibitor; both at 120-hr exposure.

Table II
Partial Nuclear Magnetic Resonance Assignments in the MI:AA Copolymer[a]

	Position	Calcd[b] δ (ppm)	Found δ (ppm)
	6	3.73 S (3 H)	3.78 S (3 H)
	4	7.2 D (2 H)	7.2–7.4 D (2 H)
	5		
	2	7.7 S (1 H)	

[a] Nmr in D_2O, Varian A-60, acid-exchange peak at 4.6 as internal reference. [b] Ref 11a, b.

MI:AA system. Figure 6 illustrates these data for a 1:1 mole feed ratio and 120-hr exposure, in the presence and absence of 100-ppm *p*-methoxyphenol inhibitor. The rate of copolymerization without inhibitor shows good linear functionality with intensity below 18,000 $\mu W/cm^2$. The exponent n in

$$R_p = kI^n$$

where R_p is the rate of polymerization, k a constant and I being either uv intensity or electrolytic curent density, was calculated from log I/log R_p plots. These log plots, which are shown in Figure 3, gave exponents, n = 1.25 (MI:AA), n = 2.12 (VI:AA), and n = 1.03 (2-MVI:AA).

The effect of added inhibitor in the case of MI:AA was that product yield decreased at the most intense uv levels. The probable explanation of this decreased yield lies with competing homopolymerization of acrylic acid which, although not determined in product yield as it is removed in the product extraction, still competes with the copolymerization. It would appear from the data that, in the presence of inhibitor at the higher uv intensities, the homopolymerization of the acrylic acid is less affected by the inhibitor than is the copolymerization. An alternative explanation for this relationship, however, is the very sharp dependence of acrylic acid homopolymerization on the uv intensity. Below 18,000 $\mu W/cm^2$ of 254 nm, the homopolymerization was slow. Above, it was observed to increase very rapidly to give very high conversions. This AA photopolymerization process is being further studied and will be reported at a later date.

Molecular weight determinations by gel permeation chromatography were not possible due to the (solvent) insolubility of the materials. Intrinsic viscosity measurements in 0.1 *N* HCl gave the data shown in Table I. The vinylimidazole (2-MVI:AA, VI:AA) photocopolymers were considerably higher in intrinsic viscosity than the MI:AA material. A comparison between the photo- and electroinitiated MI:AA products showed similar intrinsic viscosities. The behavior of the materials and their physical properties suggest that some cross-linking has occurred thereby casting some doubt as to the significance of the intrinsic viscosity data as a measure of molecular weight.

The system, as described above, has a number of unusual features that need explanation. The consistency of the copolymer content with different initiation methods and with different imidazoles is unusual, especially in view of the results of Overberger[8] which showed an 0.8:1.0 [(4)VI:AA] copolymer content in the radical-initiated copolymerization of 4(5)-vinylimidazole with AA.

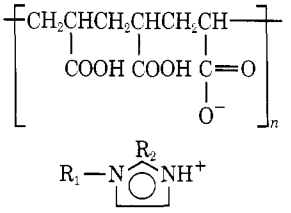
Also, the relative rate sequence MI > 2-MVI > VI, which was found with both initiation methods, is difficult to explain in that conventional polymerization processes would predict that the vinylimidazoles would be the most reactive. The imidazole ring is considerably aromatic in character and hence should not be subject to significant radical reactivity under these conditions. To examine the nature of this unusual MI:AA copolymer, the 60 MHz nuclear magnetic resonance spectrum was observed in D_2O. Using the previously published data on 1-methylimidazole,[11] an assignment was made for part of the spectrum. This is given in Table II. These data clearly indicate the presence of the 4(5)- and 1-methylimidazole protons but the absence of the 2 position imidazole protons. Reaction at the 2 position of imidazole would be consistent with the known chemistry of imidazoles; nucleophilic substitution at this position, following the protonation of the imidazole nitrogens, is well known.[12] However, a more likely explanation could be that D_2O exchange has occurred. The labile character of the 2 position in D_2O has been established.[13]

To clarify the problem of how the imidazoles are bonded into the copolymer, the ir spectra of these materials were examined. The 2-MVI–AA copolymers showed evidence of residual vinyl unsaturation at 1650 cm^{-1}, together with imidazole ring unsaturation (C=N) at 1520 and 1540 cm^{-1}. 2-MVI monomer shows vinyl absorption at 1650 cm^{-1} whereas acrylic acid unsaturation absorbs below 1640 cm^{-1}. Strong acrylic acid vinyl absorption in the 900–1000-cm^{-1} region was also absent. Attempts to remove the residual unsaturation in the copolymer by repurification failed, indicating that it did not arise from traces of residual monomers. The 2-MVI–AA spectra also showed strong absorption bands at 1410 cm^{-1} and in the 1580–1620-cm^{-1} region; these correspond to carboxylic anion (COO^-) absorption. There was also evidence of tertiary amine salt, (NH^+), absorption at 2500 cm^{-1}. The ir spectrum of the interesting 1-MI–AA copolymer showed even stronger evidence for the presence of the imidazolium polyacrylate species. The NH^+ band at 2500 cm^{-1} was strong as were the COO^- absorptions at 1410 and 1580 cm^{-1}. Imidazolium ring unsaturation (C=N) at 1540 cm^{-1} was also present.

These data suggest that the structure of these materials

(11) (a) H. A. Stabb and A. Manschreck, *Tetrahedron Lett.*, 913 (1962); (b) R. F. Borne, H. Y. Aboul-Enein, and J. K. Baker, *Spectrochem. Acta*, **28A**, 393 (1972).
(12) M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," E. Arnold, London, 1967, p 372.
(13) J. C. Salamone, private communication (1972).

involves, at least partially, the imidazolium polyacrylate entity



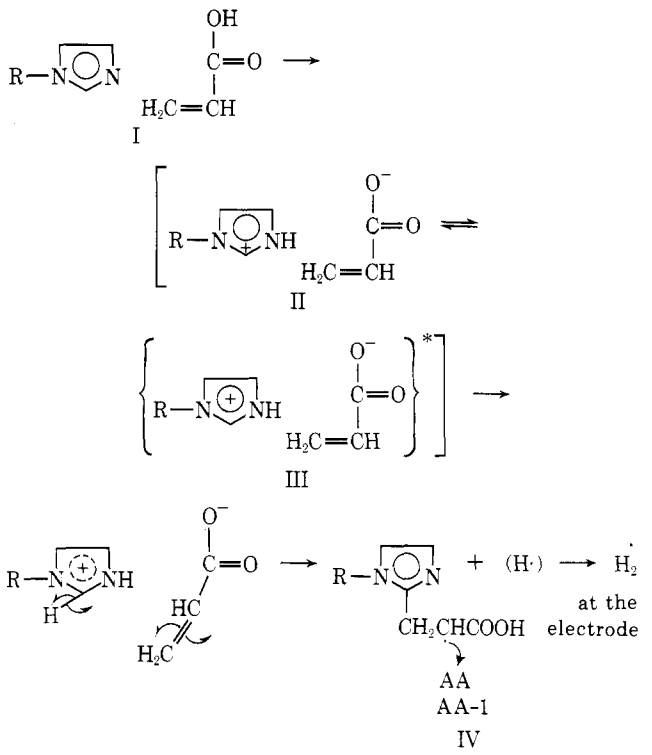
R_1 = vinyl or methyl; R_2 = methyl or H

The aqueous insolubility of this poly salt could well be the consequence of cross-linking involving the 4(5)-imidazole ring and/or the pendant vinyl groups. The strength of the NH^+ absorption in the 1-MI-AA system, *vs.* the 2-MVI-AA case, and the relative weakness of the imidazole vinyl unsaturation in the latter, indicates that some vinyl polymerization involving the imidazole could also be present. The powerful effect of the particular imidazole substituents on the initial rate of polymerization also indicates that the imidazole must play a significant role in the initiation.

Assuming the validity of the above polymer structure, it is then moderately simple to explain the unusual features of this polymerization, *viz.*, the relative rate sequence, the consistency of this rate sequence with different initiation methods, and the unusual and consistent 3:1 AA to imidazole composition.

It is reasonable to suppose that the acrylic acid protonates the basic nitrogen of the imidazole. This is consistent with the moderately basic character of alkylimidazoles (pK_a, 1-MI, gaining proton, = 7.25[14]). The complex formed, II, can then be activated with 254-nm photons or by the electrons in the electrolytic process. The result is either a photo induced electron transfer to the electron-deficient α carbon of the acrylic acid, together with substitution at the 2 or 4(5) position, or the equivalent arising out of the ionization process in the electrolytic process. The transition state (II $\rightleftharpoons$ III) then rearranges to give a radical entity (IV) and hydrogen. The polymerization initiating species is then IV and the propagation and termination are a function of the concentration and reactivity of IV and are moderately independent of the energy input that created this entity. This model is illustrated in Scheme I. It is impossible to predict the exact role of the initiating activity. It could involve ionization of I to give II or the activation of III to create an exiplex that rearranges to the polymerization initiating entity IV. It is likely that II and III exist in an equilibrium formation. The rate of polymerization in this model, given an initiation controlled polymerization, will then be a function of the equilibrium concentration of III. Hence, the rate will be directly dependent on the rate of photo- or electroactivation that produces III, and therefore the rate of polymerization will be a simple function of uv intensity or electrolytic current, as is found. Also, the equilibrium concentration of III is going to depend upon the ionic processes that create, and stabilize, III from I. The basic character of the imidazole is then the factor that, given a fixed initiation rate, determines the stability and therefore the concentration of III. Since methyl groups are electron donating while vinyl groups withdraw, and as the resonating protonated imidazolium ion is a good electronic medium for transmitting ionic substituent effects, the relative rate sequence MI > 2-MVI > VI can be explained by the effect of the substituent on the basic character of the imidazole. Since the initiation process (photons or electrons) serves only to activate preformed complexes, whose concentration is determined by the basicity of the imidazole, then it makes no difference to the relative rate sequence whether photo- or electroactivation is used.

Scheme I



The radical IV can initiate radical polymerization and the approximate 3:1, AA:imidazole, copolymer content is a function of the relative activity of the reactive entities in the system with respect to the growing chain. The reactive species in the system will be the acrylic acid monomer and the substituted imidazolium acrylate entity. The unmodified substituted imidazole is unlikely to possess significant reactivity under these conditions. All attempts at imidazole homopolymerization gave almost no reaction and most previous work confirms the sluggish properties.[4] The imidazole is therefore incorporated into the growing chain through the reactivity of the imidazolium acrylate entity. The effect of the imidazole substituent, R, on the radical reactivity of the acrylic vinyl of the imidazolium acrylate is likely to be small; therefore, the copolymer composition is independent of R. In the situation where R is a vinyl group, the reaction could proceed *via* an equivalent process using the vinyl. Protonation of the α carbon of the vinyl would create a vinylimidazolium ion, which, under the influence of the acrylic anion and after photo- or electroactivation, rearranges to give a vinylimidazolium acrylate initiating species. This mechanism is somewhat similar to that proposed by Salamone for hydrogen-transfer polymerization in 2-MVI and VI homopolymerization.[7,12] The imidazole is again incorporated into the growing chain through the radical reactivity of the vinylimidazolium acrylate competing with acrylic acid for the growing chain end. The small amount of imidazole incorporated will be the consequence of the deactivation of the imidazole and the acrylic vinyls, relative to straight acrylic acid, by the complex formation. Tazuke[5] has shown, for exam-

(14) K. Hofman, "Imidazole and Its Derivatives," Interscience, New York, N. Y., 1953, p 15.

ple, that the complexing of 1-vinylimidazoles significantly lowers the vinyl reactivity.

In the case of 2-MVI, the reaction could well proceed *via* the 1-vinyl substituent as above, or more likely *via* displacement at the 4(5) position of imidazole, in an exactly analogous manner to that described in I–IV, above. In all cases, the rate of polymerization will be determined by the basic character of the imidazole and how it stabilizes the ionic transition state (II ⇄ III). Hence the substituent can significantly affect the rate of polymerization without altering the copolymer content. Since the individual reactivity of the I–AA entity is buffered from the initiating photo- or electroprocess by the equilibrium concentration of III, then the copolymer composition will not be a function of a particular initiation mode.

This mechanism depends upon the formation of the I–AA complex (II ⇄ III). It therefore rules out the possibility of photo- and electroactivation of an uncomplexed monomer, which then interacts with the other comonomer to form the copolymerization process. If this were so, we would expect that the individual monomer reactivities would be very dependent on the substituent and the initiating process and, therefore, would result in variable composition.

The gelatinous rubbery properties found to be characteristic of the MI:AA system could possibly be the result of further reaction across the 4 or 5 ring positions. The insolubility of the resulting material, however, made nmr analysis to establish this point difficult.

This cross-linking could be further seen in the effect of heat on this rubber-like gel material. It was rapidly converted to a hard, brittle solid, insoluble in water.

This study was confined to a 1:1 mole ratio of monomers; to further elucidate the initiation and propagation mechanisms in more detail, further effort is being directed at variable feed ratio studies, together with further investigation of the polymerizability of cyclic heterosystems without vinyl substituents.

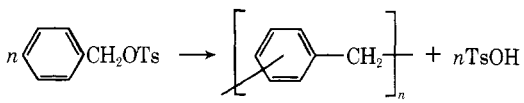
Polycondensation in the Solid State. Polymerization of Crystalline Benzyl Tosylate to Polybenzyl

Robert W. Lenz* and Ashwin M. Patel

Polymer Science and Engineering Program, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01002. *Received August 19, 1972*

ABSTRACT: The spontaneous transformation of crystalline benzyl tosylate to an amorphous polymer was studied primarily for the effect of the solid state on the kinetics of the reaction and on the structure of the polymeric products. Reaction rates in the solid state were determined by differential scanning calorimetry and by photomicrography of individual crystals on the stage of a polarizing microscope. Similar reactions of substituted benzyl tosylates in the crystalline state, including an attempted copolymerization, were also studied. The spontaneous conversion of benzyl tosylate to polybenzyl appears to be a true solid-state reaction as indicated by several aspects of the rate behavior, including anisotropy of growth within the crystal, and the crystal lattice appears to excercise some control over the products of the reaction at least in the very early stages of the polymerization. Under most conditions, however, only branched, amorphous polymers of molecular weight less than 4000 were formed in these solid-state polymerizations.

Organic chemists have long known that crystals of benzyl tosylate are difficult to keep for any length of time because they show a tendency to become converted to a "dark tarry mass" even on storage under vacuum in a desiccator.[1] This transformation has been recognized for many years as being some type of polymerization reaction that crystalline benzyl tosylate and related compounds can undergo, most likely by the reaction



Ts = *p*-$CH_3C_6H_4SO_2$

It has been assumed that the product of this transformation is polybenzyl, as shown in the equation above, but no attempt has been made in the past to study either the structure of the polymer formed or the course of the polymerization reaction itself. On the other hand, there have been literally hundreds of investigations on the preparation of polybenzyl by solution or melt polymerization reactions of various benzyl derivatives, mostly benzyl halides and alcohol.[2] Many of these studies were directed at the preparation of linear poly-*p*-benzyl, but none was successful to this end until the very recent report of the preparation of the linear, crystalline polymer by solution polymerization of benzyl chloride at −130°,[3-5] although only low yields of relatively low molecular weight polymers were formed in that study.

The prospect that the conversion of crystalline benzyl tosylate to a polymer may occur by a true solid-state polymerization reaction suggested that it may be possible to prepare the elusive linear, para-substituted polymer by this approach if the reaction in the crystal was subject to topotactic control.[6] The primary objectives of this investigation, therefore, were to ascertain whether the known transformation of crystalline benzyl tosylate to polybenzyl was a true solid-state reaction, and, if so, whether it was

*Address correspondence at Organisch-Chemisches Institut, der Universitaet Mainz, D 65 Mainz, Germany.

(1) H. Gilman and N. J. Beaber, *J. Amer. Chem. Soc.*, 47, 518 (1925).

(2) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience Publishers, New York, N. Y., 1967, pp 228–231.

(3) J. P. Kennedy and R. B. Isaacson, *J. Macromol. Sci. Chem.*, 1, 541 (1966).

(4) P. Finocchiaro and R. Passerini, *Anal. Chim.*, 58, 418 (1968).

(5) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Polym. Sci., Part A-1*, 8, 2475 (1970).

(6) E. M. Macchi, N. Morosoff, and H. Morawetz, *J. Polym. Sci., Part A-1*, 6, 2033 (1968).