

Preparation of Ultrahigh Molecular Weight Polyacrylonitrile and Its Terpolymers

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SYNOPSIS

The synthesis of high molecular weight (in excess of 10^6 million Daltons) poly(acrylonitrile) and poly(acrylonitrile-*co*-methylacrylate-*co*-itaconic acid) is described. An inverse emulsion polymerization formulation with AIBN as the initiator was used. However, polymer precipitation occurred early in the polymerization. In each case, the molecular weight distribution was surprisingly narrow ($\bar{M}_w/\bar{M}_n \sim 1.5$). Conversion vs. time plots with monomers containing the inhibitor had the "S" shape typical of emulsion polymerizations. The terpolymer composition and molecular weight were quite uniform throughout the polymerization. With inhibitor-free monomers, the initial molecular weights were very high ($\sim 3 \times 10^6$ Daltons), but gelation occurred at ca. 50% conversion. There was an inverse relationship between the monomer inhibitor content and the polymer molecular weight. It is suggested that the growing polymer radicals are occluded in the precipitated polymer particles and are terminated by inhibitor diffusing into the particles, accounting for the narrow molecular weight distribution. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The most common precursors for graphite fibers are poly(acrylonitrile) (PAN) or poly(acrylonitrile-*co*-methyl acrylate-*co*-itaconic acid). PAN and its copolymers are prepared by free-radical, aqueous suspension polymerization and the polymer molecular weight is approximately 100,000–200,000 Daltons.

Maslowski and Urbanska¹ suggested that the tenacity of PAN fibers increase monotonically with polymer molecular weight. It is anticipated that the higher the molecular weight of PAN, or its terpolymers, the higher the possible tenacity and modulus of the resulting graphite fiber. Further, a narrow molecular weight distribution should enhance the probability of achieving high-strength-high-modulus graphite fibers. While the polymerization of acrylonitrile has been extensively studied,^{2,3} there are few reports of the synthesis of ultrahigh molecular weight PAN ($>10^6$ Daltons).⁴ Here, we report the

synthesis of ultrahigh molecular weight PAN and poly(acrylonitrile-*co*-methyl acrylate-*co*-itaconic acid) terpolymers with narrow molecular weight distributions.

EXPERIMENTAL

Acrylonitrile (ACN, Aldrich, 99+ % containing 35–45 ppm 4-methoxy phenol [MOP]) and methyl acrylate (MA, Fluka, 99.5% containing 35–45 ppm MOP) were both used as received or vacuum-distilled to remove the inhibitor and stored under refrigeration until used. Itaconic acid (ITA, Fluka) was recrystallized from water; 2,2'-azobisisobutyronitrile (AIBN, Polysciences) was recrystallized from MeOH. Sodium lauryl sulfate (SLS, Fisher) and heptane (Aldrich, 99+ %, HPLC grade) were used as received. The water was deionized.

Polymerizations were conducted in either a 500 or 2000 mL, three-neck, round-bottom flask with a magnetic or motor-driven stirrer, a thermometer, and N₂ inlet and outlet tubes. ACN (and in some cases heptane) was added or ACN, MA, ITA, and

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Table I Polymerization of Acrylonitrile (with Heptane) Formulas and Data

	Parts/100 Parts Monomer						
ACN	100	100	100	100	100	100	100
AIBN	0.12	0.06	0.12	0.06	0.03	0.03	0.01
SLS	5.8	5.8	5.8	5.8	5.6	5.6	5.4
Heptane	59	59	59	59	57	58	52
Water	237	237	237	236	230	231	221
Temp (°C)	60	60	60	60	65	65	65
Time (h)	17	24	20	24	10	21	19.5
Conversion (%)	81	39	91	55	77	77	82
$[\eta]$ (dL/g)	5.33	6.29	6.10	6.82	7.19	6.91	6.38
$\bar{M}_w (\times 10^{-5})^a$	6.14	7.65	7.35	8.51	9.15	8.84	7.80

^a Calculated from $[\eta] = 2.43 \times 10^{-4} \bar{M}_w^{0.75}$.

heptane were added, followed by SLS being dissolved in water, the flask and contents heated to 60–62°C, purged with N₂ for 30 min, the temperature increased to 65°C, and AIBN dissolved in ACN injected. The resulting polymer was recovered by filtration, washed repeatedly with water, then with isopropanol, and dried in a desiccator under vacuum at 40–50°C.

Intrinsic viscosities were determined with a Ubbelohde viscometer. The PAN was dissolved in DMF and the terpolymers in DMF–LiBr (99.5/0.5 wt %) at 25°C. Flow time agreement was within 0.1 s.

FTIR spectra were obtained with a Nicolet 510P FTIR spectrometer using a KBr disk. ¹H-NMR spectra were determined with a GE 300 NMR spectrometer. The terpolymers were dissolved in (CH₃)₂SO-*d*₆ (1 w/v % concentration). The chemical shifts were referenced to TMS. The aqueous filtrate from washing the polymer was titrated with 0.1N methanolic KOH (Fisher Scientific). GPC was performed by Scientific Products, using DMF soluble polystyrene standards for calibration purposes.

RESULTS AND DISCUSSION

Polyacrylonitrile

Initially, the polymerization of ACN using a typical inverse emulsion polymerization formula (xylene or Isopar as oil phase, nonionic emulsifier) was attempted. Molecular weights (100,000–200,000 Daltons) typical of PAN prepared by conventional emulsion polymerization were obtained.

The oil phase was changed to heptane and the emulsifier to an anionic type (specifically SLS). The polymerization formulas and data for the first set

of runs employing heptane and SLS are in Table I. High degrees of conversion (80–90%) and high molecular weights 600,000–800,000 Daltons were obtained at 60°C and 0.12 phm AIBN level. Reducing the initiator level from 0.12 to 0.06 phm at 60°C did increase the PAN molecular weight (as high as 850,000) slightly, but the yield was lowered.

However, increasing the polymerization temperature to 65°C gave high yields and high molecular weights at even lower AIBN levels (0.01 and 0.03 phm). Note that the heptane levels were also somewhat lower than those noted above (see below). In all cases, the polymer precipitated at low conversions (ca. 5–10%), even at the rather high emulsifier level, indicating that a dispersion-type polymerization was involved rather than an inverse emulsion polymerization.

Another series of polymerizations were made in the absence of heptane (Table II). Again, the poly-

Table II Polymerization of Acrylonitrile (Without Heptane) Formulas and Data

	Parts/100 Monomer			
ACN	100	100	100	100
AIBN	0.03	0.03	0.03	0.11
SLS	5.7	5.7	5.8	5.5
Water	234	234	237	224
Temp (°C)	60	71	60	65
Time (h)	24	24	24	21
Conversion (%)	37	66	37	58
$[\eta]$ (dL/g)	10.19	10.29	10.19	9.69
$\bar{M}_w (\times 10^{-5})^a$	14.6	14.7	14.6	13.6
$\bar{M}_w (\times 10^{-5})^b$	19.8	19.9	19.8	18.5

^a Calculated from $[\eta] = 2.43 \times 10^{-4} \bar{M}_w^{0.75}$.

^b Calculated from $[\eta] = 0.617 \times 10^{-4} \bar{M}_w^{0.828}$.

Table III Terpolymerization Formulas and Data

	Parts/100 Monomer			
ACN	92.9	92.9	92.9	92.9
MA	6.1	6.1	6.1	6.1
ITA	1.0	1.0	1.0	1.0
AIBN	0.03	0.03	0.03	0.03
H ₂ O	220	220	220	220
SLS	5.4	5.4	5.4	5.4
Heptane	55	55	55	18
Time (h)	23	20	21.5	21
Yield (%)	68	65	56	73
[η] (dL/g)	7.81	10.49	8.92	10.09
$\bar{M}_w \times 10^{-6}$ ^a	1.07	1.59	1.28	1.51
Temp 65°C				

^a Calculated using $[\eta] = 2.34 \times 10^{-4} \bar{M}_w^{0.75}$,⁵

mer precipitated early in the polymerization. Much higher molecular weights were obtained compared to polymerizations with heptane. However, the yields were, in general, lower than the polymerizations run in the presence of heptane. Increasing the temperature to 65°C+ did provide reasonable yields (58–66%). Using the Cleland and Stockmayer⁵ relationship between intrinsic viscosity and \bar{M}_w , molecular weight values of ~ 1.4 – 1.5 million Daltons were calculated. Simionescu et al.⁶ developed a relationship for PAN of molecular weight greater than 1 million (they prepared PAN using anionic polymerization). Using their formula, the molecular weights of the PAN was ca. 2 million Daltons.

A larger-scale polymerization (500 g vs. 35 g monomer) was run in the absence of heptane at the 0.05 phm AIBN level. The conversion was 75% after 19 h reaction time and the polymer intrinsic viscosity was 10.06 dL/g.

The GPC data for this polymer are shown below:

\bar{M}_w	\bar{M}_p	\bar{M}_n	\bar{M}_z	\bar{M}_w/\bar{M}_n
1,542,000	1,682,000	1,128,000	1,864,000	1.36

The \bar{M}_w calculated using the Cleland and Stockmayer relationship is 1.51×10^6 Daltons, which agrees well with the \bar{M}_w by GPC. The low heterogeneity index (1.36) is particularly striking as it indicates that the polymer molecular weight distribution is considerably narrower than is the most probable distribution. As described below, the acrylonitrile/methyl acrylate/itaconic acid terpolymers of ultrahigh molecular weight, prepared with

the same polymerization system (including heptane), also have narrow molecular weight distributions.

Poly(acrylonitrile-co-methyl acrylate-co-itaconic acid)

As discussed above, the original intention was to employ inverse emulsion polymerization to prepare ultrahigh molecular weight PAN and terpolymers thereof. The precipitation of the PAN and its narrower molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 1.5$) indicate that the polymerization resembled a dispersion type of polymerization involving occluded propagating free radicals in precipitated polymer aggregates. Essentially the same polymerization formula was used to prepare ACN, MA, and ITA terpolymers in view of the results (high molecular weight and narrow molecular weight distribution) obtained for ACN polymerizations.

The initial terpolymerization formulas, yields, and molecular weights are in Table III. These polymerizations used monomer-containing inhibitor (4-methoxyphenol). Molecular weights between 1 and 1.5 million Daltons were obtained, and the percent conversions were varied between 56 and 63 at ca. a 20 h reaction time. Lowering the heptane level from 55 to 18 phm had little effect on the percent conversion or polymer molecular weight, contrary to the PAN polymerizations. As in the case of the PAN polymerizations, polymer precipitated in the very early stages of the polymerization, which may account for the yield and molecular weight variations for separate reactions.

To attempt to at least delay the onset of polymer precipitation, several levels of water, emulsifier, and heptane were examined using the general polymerization formula in Table IV. In essence, changes in monomer/H₂O, H₂O/emulsifier, etc., ratios were

Table IV Acrylonitrile-co-Methyl Acrylate-co-Itaconic Acid Polymerization Formula

	Parts/100 Parts Monomer
ACN	92.9 ^a
MA	6.1 ^a
ITA	1.0
AIBN	0.054
Heptane	26–55
Water	140–220
SLS	2.0–5.4

^a Unpurified.

Table V Terpolymerization Formula Variations and Data

Run #	Parts/100 Monomer			Conversion (%)	Precipitation Time (min)	[η] dL/g	$\bar{M}_w \times 10^{-6}$
	H ₂ O	SLS	Heptane				
1	220	5.4	55	32	12-17	8.25	1.15
2	220	5.4	55	18	8-14	8.68	1.23
3	220	5.4	55	37	—	8.84	1.27
4	220	3.0	55	41	8-10	8.58	1.22
5	220	3.0	31	53	4-6	9.20	1.34
6	220	2.5	26	49	4-6	9.03	1.30
7	220	2.0	21	56	4-6	9.60	1.41
8	220	3.0	55	41	8-10	8.58	1.22
9	220	2.5	55	43	6-8	8.60	1.22
10	220	2.0	55	37	5-7	8.44	1.19
11	190	5.4	55	40	10-15	8.30	1.16
12	190	5.4	48	43	6-9	8.85	1.27
13	160	5.4	55	43	6-12	8.35	1.17
14	160	5.4	40	47	6-10	8.58	1.22
15	140	5.4	55	45	8-20	8.55	1.21
16	140	5.4	35	43	5-10	9.38	1.37

Reaction temp. 65°C; reaction time 3 h.

made. Polymer precipitation times and molecular weights and percent conversions are in Table V.

The runs (1-3) at the higher water, SLS, and heptane levels had variable yields similar to the initial polymerizations (Table III). Lowering the SLS concentration (runs 4, 8, 9, 10, and 12) but maintaining the water and heptane levels gave quite uniform conversions and consistent polymer molecular weights. In fact, the results were quite reproducible

(compare runs 4, 8, and 9); however, too low an SLS concentration did result in a lower yield (run 10).

Lowering the H₂O level (140-190 phm) at constant heptane (55 phm) and SLS (5.4 phm) levels (runs 11, 13, and 15) did not affect the conversions, at least at 3 h reaction time, or the polymer molecular weight compared to the runs at the 220 phm water concentration. Lowering the heptane level appeared to have little effect on conversions but did

Table VI Conversion, \bar{M}_w and ITA Content of Copolymers vs. Time Data (Formula Same as for Run 3 in Table V)

Time (h)	Unpurified Monomers				Purified Monomers			
	Conversion (%)	[η] (dL/g)	\bar{M}_w^a ($\times 10^6$)	ITA ^b (%)	Conversion (%)	[η] dL/g	\bar{M}_w^a ($\times 10^6$)	ITA ^b (%)
1	6	7.98	1.11	0.51	9.5	18.4	3.20	0.63
2	18	8.29	1.16	0.62	32.3	19.6	3.48	0.66
3	37	8.84	1.27	0.57	62.1	10.5	1.53	0.56
4	47	8.50	1.21	0.46	—	—	—	—
5	63	8.78	1.26	0.56	77.6	9.90	1.50	0.71
8	74	8.23	1.15	0.68	83.3	7.80	1.02	0.78
10	—	—	—	—	84.5	8.93	1.11	0.76
16	84	—	—	—	—	—	—	—
22	87	7.50	1.04	0.76	—	—	—	—

^a Calculated d. using [η] = $2.34 \times 10^{-4} M_w^{0.75}$.⁵

^b Content of ITA in polymer.

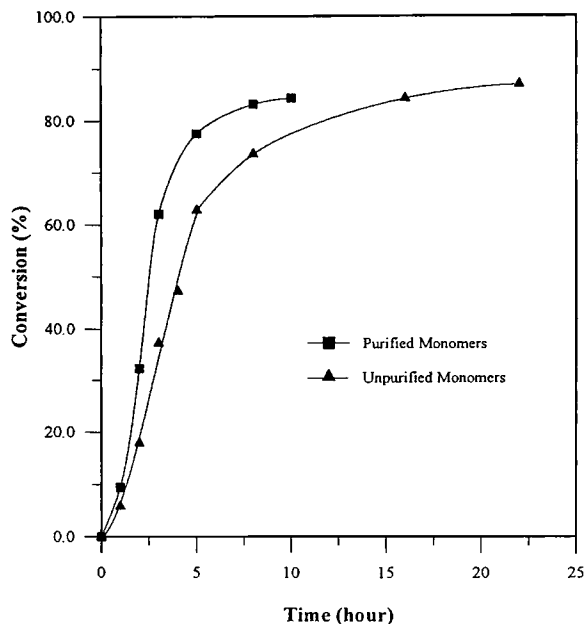


Figure 1 Conversion of copolymer vs. time data.

increase polymer molecular weights to some extent (compare runs 12, 14, and 16 to 11, 13, and 15, respectively). Lowering both the heptane and SLS levels at a constant H_2O concentration (220 phm) (runs 5–7) appeared to increase both the conversion and polymer molecular weight. However, none of the variations in monomer/ H_2O , etc., ratios markedly affected the times to polymer precipitation.

The results for run 3 were data obtained in a series of polymerizations which were terminated at various times by quenching with isopropanol. The complete set of data is in Table VI (unpurified monomers). The conversion vs. time curve (Fig. 1) has the typical "S" shape for an emulsion polymerization, suggesting that monomer diffusion into the precipitated polymer particles, containing occluded free radicals, occurs quite readily. As described below, the copolymer composition, at least as regards the ACN/MA ratio, is quite uniform, also indicating that monomer diffusion to the reaction site is not impeded. The ITA level is also quite uniform throughout the polymerization (Table VI) but lower than the monomer charge.

The \bar{M}_w values vs. conversion are plotted in Figure 2. There is little change in \bar{M}_w as the polymerization proceeds, suggesting a reasonably narrow molecular weight distribution at least up to $\sim 75\%$ conversion.

Another series of polymerizations was made using purified monomers (i.e., inhibitor-free). The results are in Table VI and the conversion vs. time and \bar{M}_w

vs. conversion data are plotted in Figures 1 and 2. The polymerization rate is faster than in the presence of inhibitor and, initially, the molecular weights are significantly higher. However, gel formed at approximately 50% conversion when the inhibitor-free monomers were used and is reflected in the molecular weight values measured at high conversions, i.e., the \bar{M}_w values are actually for the soluble portion only. The conversion vs. time curve again has the shape typical of an emulsion polymerization. The ITA content is quite constant during the polymerization.

A polymerization (run 3, Table V) was made with monomers containing inhibitors and samples removed at 5, 10, 15, and 22 h and quenched with isopropanol. After washing and drying, the samples were submitted for GPC analysis. The results are tabulated in Table VII. As was the case for the PAN homopolymerization, a narrow molecular weight distribution was obtained for the terpolymer. This suggests that the termination of occluded radicals in the precipitated polymer particles is by combination with oligomeric radicals generated in the aqueous phase and captured by the polymer particles.

The \bar{M}_w values calculated from the intrinsic viscosity data and using the Cleland and Stockmayer relationship⁵ agree quite well with the GPC values even though this relationship was generated for PAN

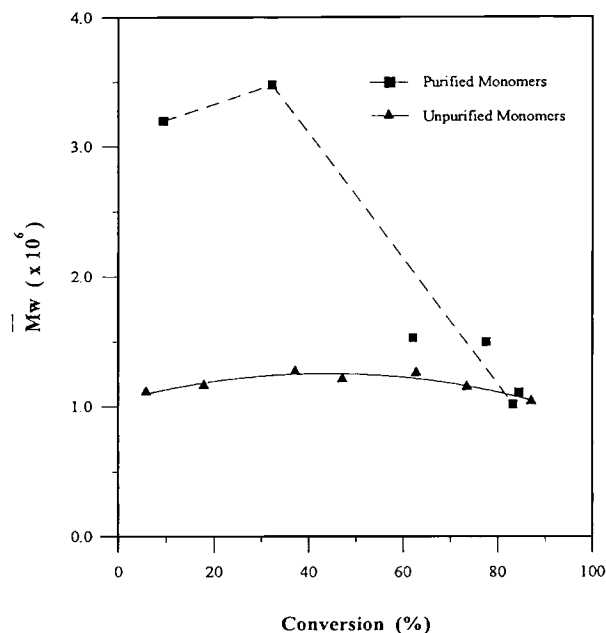


Figure 2 Molecular weight of copolymer vs. conversion data.

Table VII GPC Analytical Data

Reaction Time (h)	$\bar{M}_w \times 10^6$	$\bar{M}_n \times 10^6$	\bar{M}_w/\bar{M}_n	$[\eta]$ dL/g	$\bar{M}_w \times 10^6$ ^a
5	1.625	1.155	1.46	11.9	1.88
10	1.608	1.062	1.51	10.8	1.66
15	1.519	0.9695	1.56	11.2	1.74
22	1.507	0.9508	1.58	11.0	1.69

^a Calculated from $[\eta] = 2.34 \times 10^{-4} M_w^{0.75}$.

in DMF while the solvent for the terpolymer is DMF/LiBr (99.5/0.5 wt %).

Figure 3 is the ¹H-NMR spectrum of the terpolymer sampled at 22 h reaction time. The methine and methylene protons of the PAN segments are at 3.16 and 2.04 ppm, respectively. The CH₃ signal due to the methyl acrylate ester groups is at 3.70 ppm. Unexpectedly, it is a triplet, suggesting repulsion by adjacent nitrile groups, forcing the ester group to adopt a conformation which brings the methyl group adjacent to a backbone methylene group. The relative intensities of the signals at 2.04 and 3.70 ppm were compared for the 5, 8, and 22 h samples to obtain a semiquantitative estimate of the MA content vs. conversion. The data (Table VIII) indicate that the MA content of the polymer is quite uniform as a function of reaction time.

Another series of terpolymerizations were made (using purified monomers and polymerization formula 3, Table V) and quenched at various times with isopropanol. After isolation of the polymer, FTIR spectra were obtained of the terpolymers. A typical FTIR spectrum (1 h reaction time) is shown in Figure 4. The ratios of the peak heights of the carbonyl absorbance (at 1732 cm⁻¹) and the nitrile absorbance (at 2243 cm⁻¹) are listed in Table IX. It may be seen that the peak ratio or the polymer composition reflects the *r*₁ and *r*₂ values for ACN and MA (0.67 and 1.26, respectively) and the initial monomer concentrations. The values show that the ACN/MA ratio in the terpolymer is reasonably uniform up to high conversions (ca. 85%), again suggesting, as stated above, that monomer diffusion into the precipitated polymer particles is unimpeded.

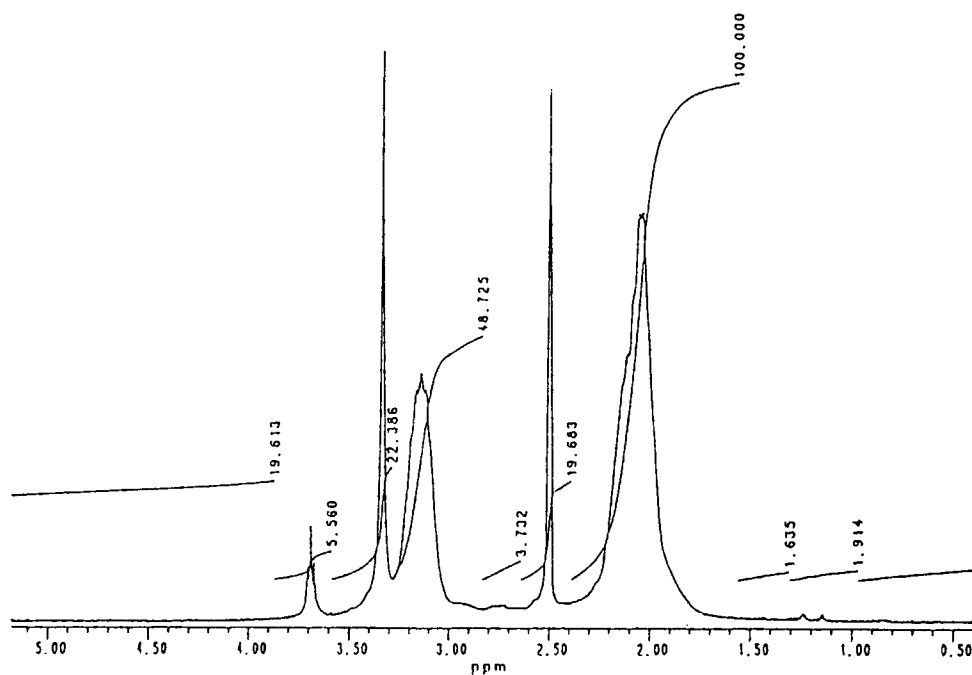


Figure 3 ¹H-NMR spectrum, poly(ACN-co-MA-co ITA).

Table VIII Poly(acrylonitrile-co-Methylacrylate-co-itaconic acid) Methine/Methylene Resonance Ratios

Reaction Time (h)	Ratio ($\times 10^2$)
5	4.4
10	4.8
22	5.6

The ITA content of the copolymer also increases with conversion up to ca. 85% conversion (Table IX) but never attains 1% (the initial concentration of ITA in the reaction mixture), probably due to its relatively high water solubility.

Higher yields and molecular weights were obtained in the homopolymerization of ACN in the absence of heptane. However, to obtain reasonable polymer yields for the terpolymerization, it was necessary to run the polymerizations in the presence of heptane (at least 26 phm, Table V). At present, we have no suggestions for the role of heptane in these polymerizations.

The terpolymers used to study the relative rates of comonomer incorporation were prepared using purified monomers. As noted above, gelation started to occur at ca. 50% conversion in contrast to the polymerizations using unpurified monomers, where, in the latter case, the terpolymers were soluble in

DMF/LiBr up to 85% conversion. This effect has been observed earlier.⁴

To further examine the effect of the inhibitor (4-methoxyphenol, MOP), a series of polymerizations were made using the formulation of run 3 (Table V) but containing various concentrations of MOP (Table X) after the inhibitor was first removed from the monomers by vacuum distillation. Both the rate and \bar{M}_w are significantly reduced as the concentration of inhibitor is increased and the polymers were all soluble.

Heterophase polymerizations involving polymers not soluble in their own monomers (e.g., ACN) and emulsion polymerization systems are, as pointed out by Murray and Piirma,⁷ very complex. There is not only segregation between the monomer and continuous phase but also between polymer and monomers. Thus, the polymer precipitates early in the polymerization.

Thomas and Pellon⁴ and Bamford and Jenkins^{8,9} discussed the kinetics of the heterogeneous polymerization of ACN and concluded that the propagating free radicals become occluded in polymer aggregates which reduces the rate of termination. Indeed, Thomas and Pellon reported intrinsic viscosities of poly(ACN) in DMF similar to those reported here but did not discuss the poly(ACN) heterogeneity. They proposed a kinetic scheme that involves the possibility of unimolecular chains by a process of radical burial. They also suggested that occluded radicals may be "accessible only to the smallest radicals."

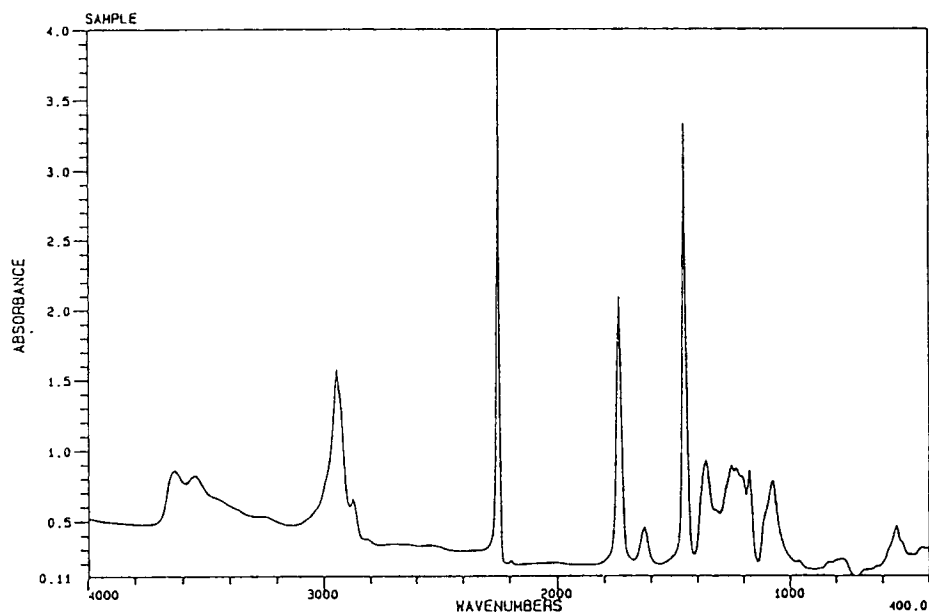
**Figure 4** FTIR spectrum of poly(ACN-co-MA-co-ITA).

Table IX Ratio of Infrared Absorbance Peaks and ITA Content of Terpolymer vs Conversion

Reaction Time (h)	Conversion (%)	Peak Ratio (1732/2243 cm^{-1})	ITA Content (Wt %)
1	12.6	0.625	0.56
2	36.1	0.654	0.61
3	66.4	0.676	0.60
5	71.4	0.631	0.63
10	84.5	0.733	0.79
15	85.3	0.766	0.89
22	85.5	0.762	0.88

It is well known that termination by combination tends to give a polymer molecular weight distribution ($\bar{M}_w/\bar{M}_n \sim 1.5$) that is narrower than the most probable distribution. The present results suggest that polymer initiation occurs in the aqueous phase, and after a growing polymer radical [either poly(ACN) or the terpolymer] reaches a certain size, it precipitates. The polymerization then proceeds by monomer diffusion into the precipitated polymer particles. The particles may also capture small polymer radicals and initiator radicals from the aqueous phase which terminate the occluded radicals by combination.

However, the results for the terpolymerizations employing various levels of MOP (Table X) suggest the possibility the inhibitor diffuses from the monomer phase to the precipitated polymer particles and terminates the occluded polymer radicals. This would result in a polymer molecular weight distribution narrower than the most probable. In the absence of an inhibitor (Table VI), the initial molecular weight are over 3×10^6 Daltons and gelation occurs early in the polymerization. These results support Thomas and Pellon's suggestion that the occluded polymer radicals may be "accessible only to the smallest radicals." In the inhibitor-free polymerizations, the rate of termination is relatively low as only small polymer radicals may terminate growing

occluded polymer radicals in the precipitated polymer particles. (Of course, initiator radicals can also participate in the termination process.) However, the monomer can enter the polymer particles, resulting in continued polymer growth and crosslinking after the polymer attains a certain size.

Inhibitor molecules can readily enter the polymer particles, terminating the occluded growing polymer radicals. Polymer growth ceases until another initiator radical is captured, accounting for the reduced polymerization rates in the presence of MOP. Likewise, the polymer chain length is sufficiently reduced so gelation does not occur. In essence, in the presence of inhibitor, the process involves unimolecular chains, as suggested by Thomas and Pellon, resulting in a relatively narrow molecular weight distribution.

CONCLUSIONS

The results of this investigation emphasize the complexities of emulsion-type polymerizations involving polymers insoluble in their monomers, and in such cases, a dispersion-type polymerization is involved. However, it is possible to obtain high molecular weight (in excess of 1 million Daltons) PAN and PAN terpolymers. The propagation step in-

Table X The Effect of Inhibitor on the Terpolymerization

MOP Concn phm $\times 10^{-3}$	Time (h)	Conversion (%)	$[\eta]$ dL/g	\bar{M}_w ($\times 10^6$)
4.3	3	40.4	8.77	1.25
8.6	3	34.5	7.94	1.10
19	3	24.4	6.40	0.82
94	3	19.5	5.06	0.60
3.5-4.5 ^a	3	37.2	8.84	1.27

^a Monomer as received.

volves growing free radicals occluded in precipitated polymer aggregates which are readily accessible to the monomer. The termination step is by combination as the occluded radicals are accessible to small polymer radicals and/or initiator fragments, resulting in relatively narrow molecular weight distribution. For monomers containing inhibitor(s), termination may occur by the inhibitor entering the precipitated polymer particles. In this case, unimolecular chains are involved, which also results in a narrow polymer molecular weight distribution.

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Received February 21, 1995

Accepted June 6, 1995