

Synthesis of Methylmethacrylate/acrylonitrile Organosol Copolymer

by

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ABSTRACT

Characterization of MMA/AN organosol copolymer and subsequent comparison with the prior art latex copolymers has been accomplished. By means of NMR analyses, we found both types of copolymers to be random. The GPC analyses show that the organosol copolymers have a significantly broader MW spread than latex copolymers. This is due to the low MW stabilizer which is present as a physical mixture. As a result, the MW distribution is bimodal. Fractionation of a typical organosol copolymer yields a low MW (33,000-100,000), MMA rich fraction and a high MW (250,000-330,000), AN rich fraction. Solubility-wise, the organosol copolymers are readily soluble in the lacquer solvent MEK to give a colorless film. The prior art copolymers, however, were incompletely soluble and gave yellow, hazy film.

Organosol, in a broad sense, is defined to be a suspension of colloidal particles in an organic medium which is not capable of dissolving the dispersed particles at ordinary temperatures. In this report, we will mean by organosol a polymeric suspension of submicron size which possesses the unusual combination of a high solid content (50%) and a low viscosity (10 cps). As such, the organosol based finishes are readily sprayable with conventional spray guns with high solid delivery. The shelf life of these organosols are also extremely good due to the incorporation of polymeric stabilizer. This report summarizes the characterization of MMA/AN organosol stabilized by P2EHA→PMMA graft copolymer.

A stable dispersion of MMA/AN copolymer particles in an inexpensive hydrocarbon media as described in this report can be prepared with a variety of polym-

eric stabilizers under varying process conditions. For example, the polymerization media can be commercial heptane, mixture of hexane plus heptane or naphtha. The polymerization proceeds quite smoothly with or without inhibitor normally present in the monomer. The organosols can also be prepared in a batch or a continuous reactor with a high degree of conversion (98%+).

In the course of work, therefore, it became apparent that a standardization of a process is necessary in order to obtain reproducibility and reliability. After a considerable number of runs, we have decided upon a standard procedure which consists of the following three steps:

- Reflux stage without monomers.
- Seed polymerization stage.
- Main polymerization stage.

With this scheme, stable MMA/AN copolymer dispersions with varying AN contents were obtained with ease. The operating conditions and the analytical results are shown in table I.

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TABLE 1. MMA/AN Organosol Copolymerization

Run No.	MMA/AN in Feed	Solid (%)	Penetrometer Values of Cast Film (T _g °C)		Color	Lacquer Film			Particle Size (micron)
			Organosol/BCA	Lacquer		Elong %	Tensile (×10 ³ psi)	Init. Mod. (×10 ³ psi)	
102	70/30	48.5	86	87	Clear	4.1	6.5	217	
94	80/20	44.4	70	85	"	7.2	7.6	204	0.15-0.3
96	80/20	46.7	82	—	"	1.9	3.5	205	0.7-0.9
100	90/10	52.2	72	88	"	4.4	6.4	195	—
116	78/22	33.3	—	—	Gray	—	—	—	0.01-0.05

Two aqueous emulsion copolymers of MMA/AN were also prepared using redox catalysts (see Experimental Details section) for comparison. The latex was prepared according to the Firestone patent at 40°C which gave high MW MMA/AN (85/15). The product compositions were determined by nitrogen analysis.

In the case of organosol copolymers, the dispersions were then converted either into an organosol or a lacquer film for characterization. The organosol films were prepared by baking the mixture of stripped down organosol, coalescing aid and a polymeric, silicone leveling agent for one hour at 150°C. The lacquer films were obtained by dissolving the air

dried polymer in MEK and subjecting it to the same baking schedule. The results of characterizations are discussed below.

SOLUBILITY AND COLOR

Most polymers and copolymers of acrylonitrile are "off-white" in color and become yellowish when they are subjected to mild coloring conditions (Refs. 1, 2). It is also known that the comonomer introduced into the PAN chain also increase the solubility (Ref. 2). Both of these properties are important from the standpoint of clear lacquer formulation with good gloss. Our findings are summarized in Table 2.

TABLE 2. Comparison of organosol with latices

Run No.	MMA/AN		Type	Solubility at R. T.		Color of Lacq. Soln.
	Feed	Prod.		20% in MEK	BCA	
102	70/30	74/26	Org.	Soluble	...	Clear
96	80/20	84/16	"	"	...	"
100	90/10	90/10	"	"	...	"
84	40/60	40/60	"	Insol.	...	Clear, Yellowish
114	70/30	72/28	Latex	"	Insol.	Hazy Yellow*
116	80/20	85/15	"	"	"	Hazy Gray*

* Emulsifier not removed.

The solubility of our organosol, however decreases markedly when the AN content is higher than 30%. In order to compare some of the mechanical properties mentioned in the Firestone patent, we have molded test bars (5" × 1/2" × 1/8") with our organosols at 195 C/1000 psi./4min. Thin films (3-7mils) were also pressed at the same conditions. The results

show that the yellowness is readily observable in test bars when the AN content is higher than 20%, while the color does not stand out in the case of thin films with AN contents of up to 50%. These data give some indication of the color of clear lacquer under overbake conditions and the detectability of color as a function of sample thickness.

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA

NMR spectroscopy, within the past few years, has

been used to characterize the polymer microstructure (Ref. 3). With this technique, we were able to pick out a triad ratio of MMA-MMA-MMA, AN-MMA-MMA and AN-MMA-AN (Figure 1.) The triads

are formed due to the influence of the neighboring molecules on COOCH₃ resonance of MMA in the polymer chain. The area ratios in essence then give a quantitative measure of the molecular arrangement. The MMA-MMA-MMA fraction observed in the case of organosol copolymer include the contribution from the P2EHA→PMMA(70/30) graft copolymer stabilizer. The maximum possible contribution, however, is 1.5% since the stabilizer in the feed is at 5% of the monomer charge.

The comparison of the spectra of organosol and emulsion copolymer indicate that both are random in its molecular arrangement. Furthermore, differentiation of the two types of polymers, organosol and latex, based on the degree of randomness is difficult if not impossible (Ref. 4).

The samples for NMR were dissolved in *o*-dichlorobenzene at 150°C at 15% concentration. The ppm. magnetic field strength is calculated with respect to the

internal reference of hexamethylene disiloxane. The summary of triad ratios are shown in Table 3.

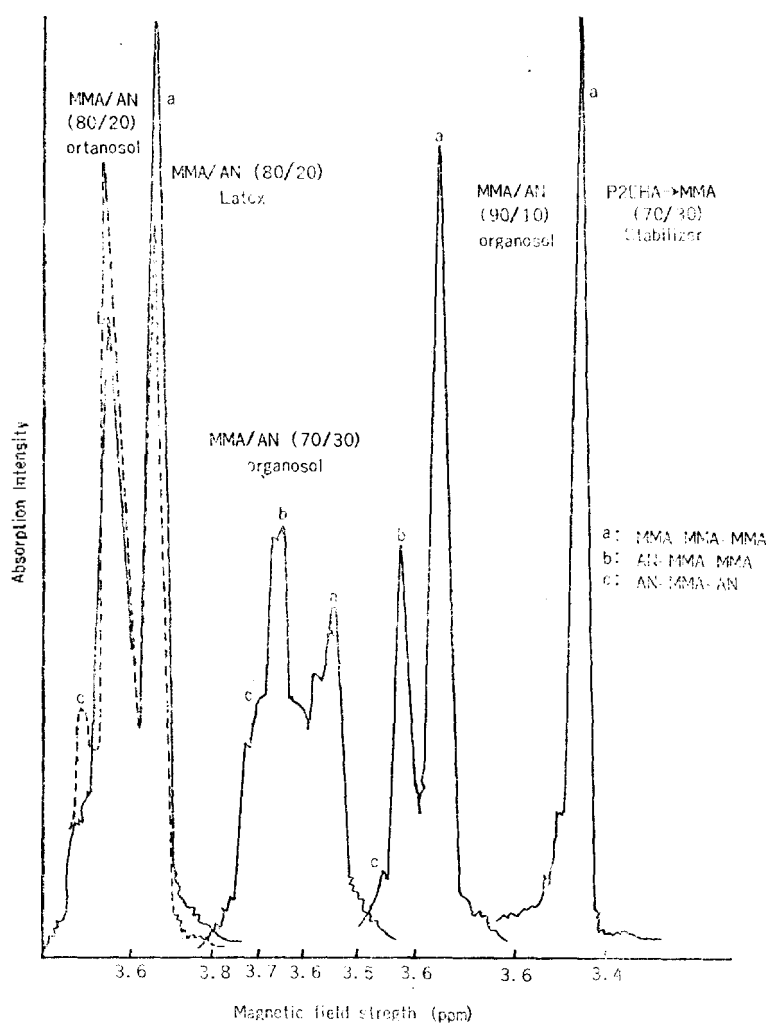


Fig. 1. Proton NMR Triads

TABLE 3. NMR analyses

Run No.	Wt. Ratio MMA/AN in Feed	Type	Triad Sequence			Mol. Ratio MMA/AN in Prod. by N Anal.	Mol. Ratio MMA/AN in Prod. by NMR
			M-M-M	A-M-M	A-M-A		
102	70/30	Org.	33	37	30	60/40	68/32
96	80/20	"	40	44	16	72/28	75/25
98	80/20	"	41	43	16	72/28	75/25

100	90/10	"	58	33	9	81/19	83/17
114*	70/30	Latex					
116	80/20	"	49	38	13	75/25	79/21

* The copolymer was insoluble in *o*-dichlorobenzene.

GEL PERMEATION CHROMATOGRAPHY

The molecular weight distributions of the copoly-

mers were measured with the Waters Associates' equipment by D. D. Bly of duPont. The results are shown in Figs. 2, 3, and Table 4.

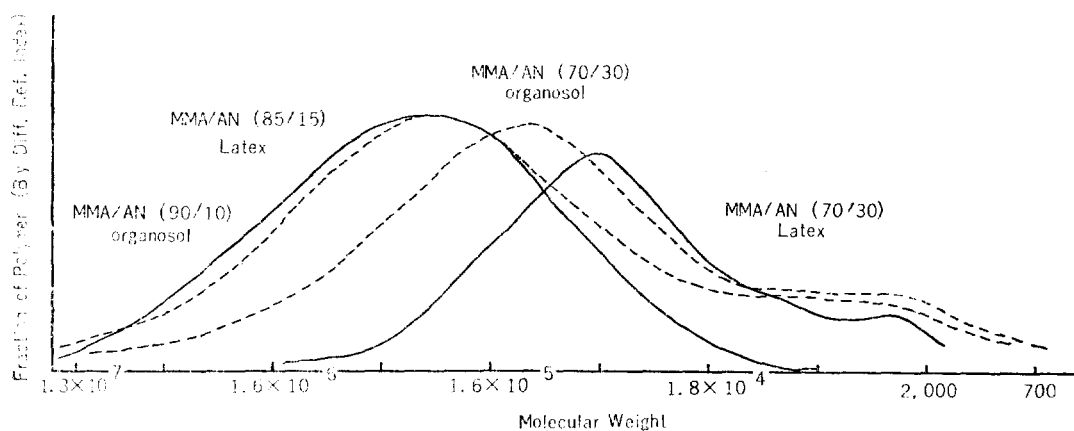


Fig. 2. Molecular Weight Distributions by Gpc

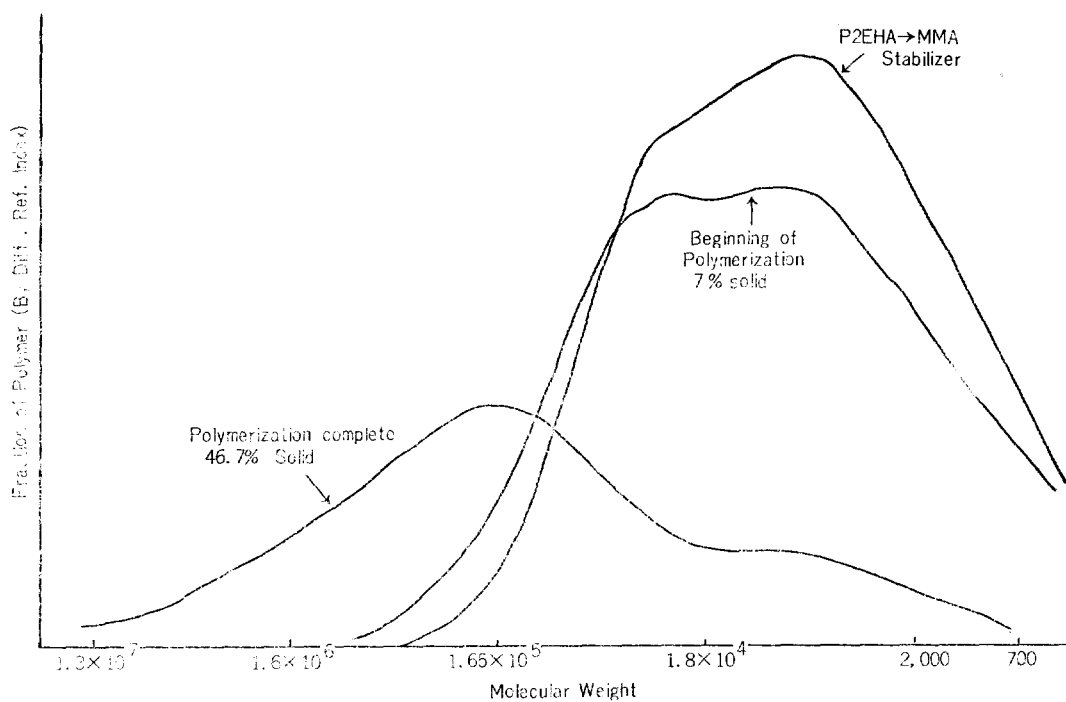


Fig. 3. Molecular Weight changes During Organosol Polymerization

TABLE 4. GPC analyses

Run No.	MMA/AN	Type	M_w	$d = \overline{M}_w / \overline{M}_n$
102	70/30	Org.	125,000	2.9*
94	80/20	"	170,000	3.2*
100	90/10	"	300,000	3.2*
114	70/30	Latex	63,000	2.1
116	80/20	"	330,000	3.1

* Low MW tail was not included in dispersity calculation.

Examination of the distributions show that all of our organosol exhibit a low MW tail. This low MW material is the (P2EHA→PMMA) graft copolymer stabilizer. Figure 3 in particular indicates little additional grafting when the stabilizer is exposed to the MMA/AN monomer along with the 'AIBN' initiator. The organosol end product, therefore, is a physical mixture of MMA/AN and (P2EHA→PMMA) copolymers.

The presence of this low MW tail then gives a product with MW range of a few hundred to 10 million which is broader than any of the latices prepared. This spread is reflected in the higher value of dispersity for our organosol copolymer. The possibility of this low MW polymer functioning as a polymeric plasticizer is important.

FRACTIONAL PRECIPITATION AND EXTRACTION

Although the GPC technique can distinguish the differences of polymer sizes, it does not fractionate them according to their chemical composition. In order to examine the composition of the polymer, therefore, the organosol copolymer dissolved in MEK were titrated with varying amount of toluene. The resulting solutions after equilibration were then centrifuged to separate the precipitated polymer for analysis. The results obtained with 0.5gr. of MMA/AN (80/20) polymer are shown in Figure 4 and Table 5.

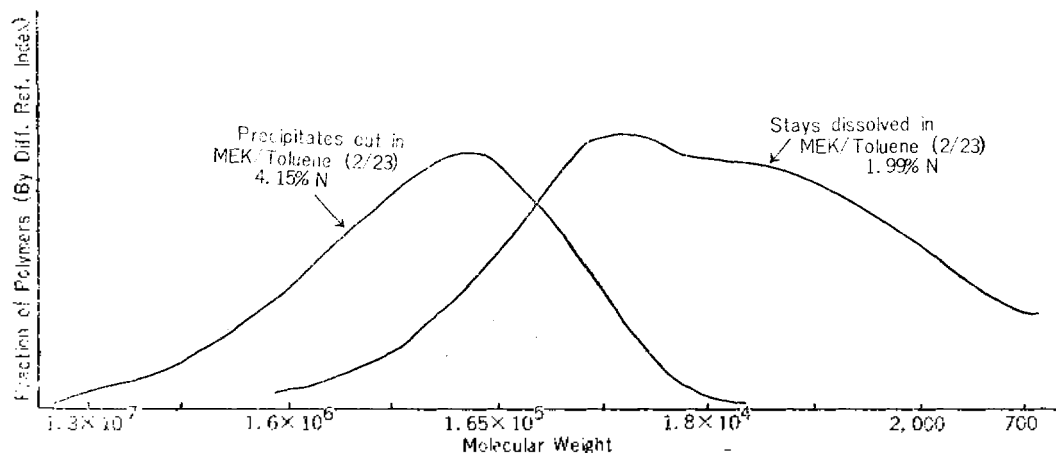


Fig. 4. Fractionation of MMA/AN (80/20) in MEK by Titrating with MEK/Toluene

TABLE 5. Fractional precipitation

MEK/Tol. (ml.)	Precipitated Polymer				Polymer In Solution			
	(gr.)	(N%)	M_w	d	(gr.)	(N%)	M_w	d
2/23	0.48	4.2	250,000	2.7	0.13	2.0	33,000	4.6
5/20	0.19	4.9	330,000	2.5	0.32	2.5	100,000	3.2

The organosol copolymer was also subjected to extraction with benzene to see if homopolymerization of MMA takes place. Bulk of the copolymer swelled although some extraction could be noted by the yellowness of the benzene phase. IR spectra of the polymers in both phases, however, differed considerably from PMMA and PAN spectra. We therefore conclude little homopolymerization of MMA to take place in the course of organosol copolymerization.

INFRARED SPECTRA

A detailed infrared study of MMA/AN copolymer microstructure by Schmolke(Ref. 5) was found to be useful in our work. Specifically, the run length of MMA-MMA...chain within the copolymer was plotted against AN mol. % (Fig. 5) On a statistical basis, the probability of finding an MMA block is related to the band intensity ratio of E1060/E840. The plot, however, did not bring out differences between the organosol and latex copolymer

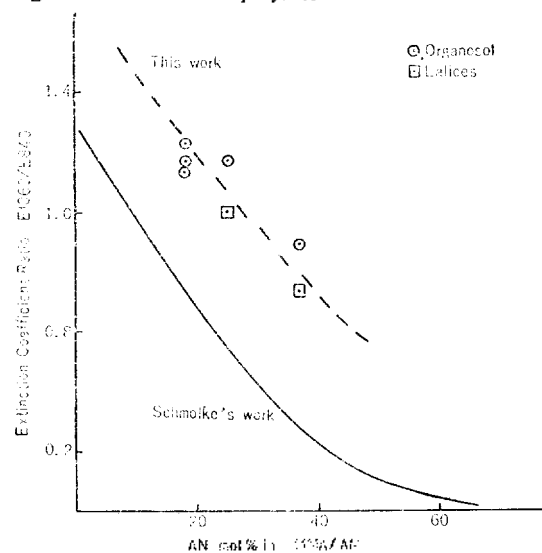


Fig. 5. Decrease in Infrared Intensity of Syndiotactic MMA Bond by AN

EXPERIMENTAL DETAIL

a. MMA/AN Organosol

Reflux Stage

50gr of Heptane

5gr of PZEHAA-PMMA stabilizer

Seed Stage

5gr stabilizer

100gr heptane

123gr MMA(with inhibitor)

30gr AN(with inhibitor)

0.1gr dodecyl mercaptan

1.0gr AIBN

Pump in the above mixture for 12.5min. at 4ml/min. and maintain 70°C for 2 hrs.

Polymerization Stage

Pump in the remainder and maintain 70°C for 3. hrs.

b. MMA/AN Emulsion latex according to

U. S. 2,929,795(Firestone)

Material used:

Water(deionized, deoxygenated)	200.00gr
"Aquarex" ME	2.0
Potassium Persulfate	0.5
Sodium Bicarbonate	0.25
MMA	78.0
AN	22.0
Dodecyl mercaptan	0.2

Procedure-Purge 1 liter reaction kettle with N_2 . Dissolve "Aquarex" ME, persulfate and bicarbonate in 200gr. of water. Bring the content to 40°C under N_2 purge. Introduce monomers and maintain the kettle at 40-45°C for 20 hrs.

REFERENCES

- 1) E. H. Riddle, *Monomeric Arylic Esters*, Reinhold. Pub. Co., N. Y. 1954, p. 79

- 2) G. Ham, *Copolymerization*, Interscience Pub., N. Y. (1964), p. 576
- 3) R. C. Ferguson, *High Freq. NMR Spectra of Polymers*, *Trans. of N. Y. Acad. of Sci.*, II, 26, No. 44, 495-501 (1967)
- 4) R. C. Ferguson, *Private Communication*
- 5) R. Schmolke, "Characterization of Polymers. IR Spectroscopic Investigation of the Sequence-Length Distribution in AN-MMA Copolymers", *Faserforschung und Textiltechnik*, 19, 589(1965)

GLOSSARY

MMA—Methyl methacrylate
AN—Acrylonitrile
2EHA—2-ethylhexylacrylate
MEK—Methyl ethyl ketone
BCA—Butyl "Cellesolve" acetate