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 high solid content (50%) and a low viscosity (10 cP). 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 polymeric stabilizers under varying process conditions. For example, the polymerization media can be commercial heptane, mixture of heptane plus butylene 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 1.
TABLE 1. MMA/AN Organosol Copolymerization

<table>
<thead>
<tr>
<th>Run No.</th>
<th>MMA/AN in Feed (%)</th>
<th>Solid (°)</th>
<th>Penetrometer Values of Cast Film (Tg°C)</th>
<th>Organosol/BCA Lacquer</th>
<th>Color</th>
<th>Lacquer Film</th>
<th>Film Solubility at R.T. (%)</th>
<th>Elong % (×10’psi)</th>
<th>Mech. Mod. (×10’psi)</th>
<th>Particle Size (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>70/30</td>
<td>48.5</td>
<td>86</td>
<td>87</td>
<td>Clear</td>
<td>4.1</td>
<td>6.5</td>
<td>217</td>
<td>0.13-0.3</td>
<td>0.91-0.05</td>
</tr>
<tr>
<td>94</td>
<td>80/20</td>
<td>44.4</td>
<td>70</td>
<td>85</td>
<td></td>
<td>7.2</td>
<td>7.6</td>
<td>204</td>
<td>0.7-0.9</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>80/20</td>
<td>45.7</td>
<td>82</td>
<td>88</td>
<td></td>
<td>1.9</td>
<td>3.5</td>
<td>206</td>
<td>0.1-0.9</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>90/10</td>
<td>52.2</td>
<td>72</td>
<td>88</td>
<td></td>
<td>4.4</td>
<td>6.4</td>
<td>195</td>
<td></td>
<td>0.01-0.05</td>
</tr>
<tr>
<td>116</td>
<td>78/22</td>
<td>33.3</td>
<td>—</td>
<td>—</td>
<td>Gray</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
<td>0.01-0.05</td>
</tr>
</tbody>
</table>

Two aqueous amulsion 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 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 comonomers 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 latexes

<table>
<thead>
<tr>
<th>Run No.</th>
<th>MMA/AN in Feed (%)</th>
<th>Prod. (%)</th>
<th>Type</th>
<th>Solubility at R.T. (%)</th>
<th>Color of Lacq. Soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>70/30</td>
<td>74/26</td>
<td>Org.</td>
<td>Soluble</td>
<td>Clear</td>
</tr>
<tr>
<td>94</td>
<td>80/20</td>
<td>84/16</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>100</td>
<td>90/10</td>
<td>90/10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>84</td>
<td>70/60</td>
<td>40/60</td>
<td>&quot;</td>
<td>Insol.</td>
<td>Clear, Yellow*</td>
</tr>
<tr>
<td>114</td>
<td>70/30</td>
<td>72/28</td>
<td>Latex</td>
<td>&quot;</td>
<td>Insol.</td>
</tr>
<tr>
<td>116</td>
<td>70/30</td>
<td>85/15</td>
<td>&quot;</td>
<td>&quot;</td>
<td>Hazy Gray*</td>
</tr>
</tbody>
</table>

* Emulsifier not removed.

The solubility of our organosol, however, decreases markedly when the AN content is higher than 50%. In order to compare some of the mechanical properties mentioned in the Firestone patent, we have molded test bars (5/0 × 2/2 × 1/8") with our organosols at 195°C/1000 psi, 4 min. Thin films (3-7 mils) 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 lacquers under overbake conditions and the determinability 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 hexamethylen disiloxane. The summary of triad ratios are shown in Table 3.

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**TABLE 3. NMR analyses**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Wt. Ratio MMA/AN in Feed</th>
<th>Type</th>
<th>Triad Sequence</th>
<th>Mol. Ratio MMA/AN in Prod. by N Anal.</th>
<th>Mol. Ratio MMA/AN in Prod. by NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>70/30 Org.</td>
<td>M-M-M</td>
<td>33 37 30</td>
<td>60/40</td>
<td>68/32</td>
</tr>
<tr>
<td>98</td>
<td>80/20 n</td>
<td>M-M-M</td>
<td>40 44 16</td>
<td>72/26</td>
<td>75/25</td>
</tr>
<tr>
<td>98</td>
<td>80/20 n</td>
<td>M-M-M</td>
<td>41 43 16</td>
<td>72/26</td>
<td>75/25</td>
</tr>
</tbody>
</table>

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The copolymer was insoluble in o-dichlorobenzene.

**GEL PERMEATION CHROMATOGRAPHY**

The molecular weight distributions of the copolymers were measured with the Waters Associates' equipment by D. D. Bly of duPont. The results are shown in Figs. 2, 3, and Table 4.
Synthesis of Methylmethacrylate/acrylonitrile Organosol Copolymer

TABLE 4. GPC analyses

<table>
<thead>
<tr>
<th>Run No.</th>
<th>MMA/AN</th>
<th>Type</th>
<th>$M_w$</th>
<th>$d=M_w/M_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>70/30</td>
<td>Org.</td>
<td>125,000</td>
<td>2.9*</td>
</tr>
<tr>
<td>94</td>
<td>80/20</td>
<td>ft</td>
<td>170,000</td>
<td>3.2*</td>
</tr>
<tr>
<td>100</td>
<td>90/10</td>
<td>ft</td>
<td>300,000</td>
<td>3.2*</td>
</tr>
<tr>
<td>114</td>
<td>70/30</td>
<td>Latex</td>
<td>63,000</td>
<td>2.1</td>
</tr>
<tr>
<td>116</td>
<td>80/20</td>
<td>ft</td>
<td>330,000</td>
<td>3.1</td>
</tr>
</tbody>
</table>

* Low MW tail was not included in dispersity calculation.

Examination of the distributions show that all of our organosol exhibits 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 0.5 gr. of MMA/AN (80/20) polymer are shown in Figure 4 and Table 5.

![Fractionation of MMA/AN (80/20) in MEK by Titrating with MEK/Toluene](image)

**Fig. 4. Fractionation of MMA/AN (80/20) in MEK by Titrating with MEK/Toluene**
TABLE 5. Fractional precipitation

<table>
<thead>
<tr>
<th>MEK/Tol. (ml.)</th>
<th>Precipitated Polymer</th>
<th>Polymer In Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(gr.) (N%) M_n d</td>
<td>(gr.) (N%) M_n d</td>
</tr>
<tr>
<td>2/23</td>
<td>0.48 4.2 250 000 2.7</td>
<td>0.13 2.0 33 000 4.6</td>
</tr>
<tr>
<td>5/20</td>
<td>0.19 4.9 330 000 2.5</td>
<td>0.32 2.5 100 000 3.2</td>
</tr>
</tbody>
</table>

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.

EXPERIMENTAL DETAIL

a. MMA/AN Organosol
   Reflux Stage
   50gr of Heptane
   5gr of PZEHA--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 12.5 min. 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. 2,928,795 (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 N₂. Dissolve “Aquarex” ME, persulfate and bicarbonate in 200gr. of water. Bring the content to 40°C under N₂ purge. Introduce monomers and maintain the kettle at 40–45°C for 20 hrs.

REFERENCES
Synthesis of Methylmethacrylate/acrylonitrile organosol Copolymer

4) R. C. Ferguson, Private Communication

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