

# Polymer Cation Effect on the Viscosity of Aqueous Dispersions of Acrylatemethacrylates, Water-Insoluble Copolymers

In film coating procedures with polymeric materials, it is desirable that coating liquid be considerably fluid because viscous liquids cause blocking of spray nozzles and do not dry readily. Aqueous solutions of hydrophilic (water-soluble) polymers are usually very viscous even at the moderate concentrations in which they are employed as coating fluids. Now aqueous dispersions of cationic acrylate-methacrylates, (water-insoluble copolymers) can be prepared by a coacervation technique<sup>1</sup> and by direct dispersion in hot water.<sup>2</sup> Such dispersions contain polymer-rich droplets of submicroscopic sizes and cannot be precipitated by normal centrifugation; but they are highly sensitive to electrolytes.<sup>3</sup> They form films having equivalent barrier property to organic (ethanol) cast film coatings<sup>1</sup> and thus have protective and controlled release applications.<sup>2</sup> Presence of cationic groups in their structure causes mutual repulsiveness of polymer chains leading to a high fluidity of their dispersion. In this study the viscosities of these dispersions are correlated to their polymer cation content and compared with the viscosity of a water-soluble polymeric colloid.

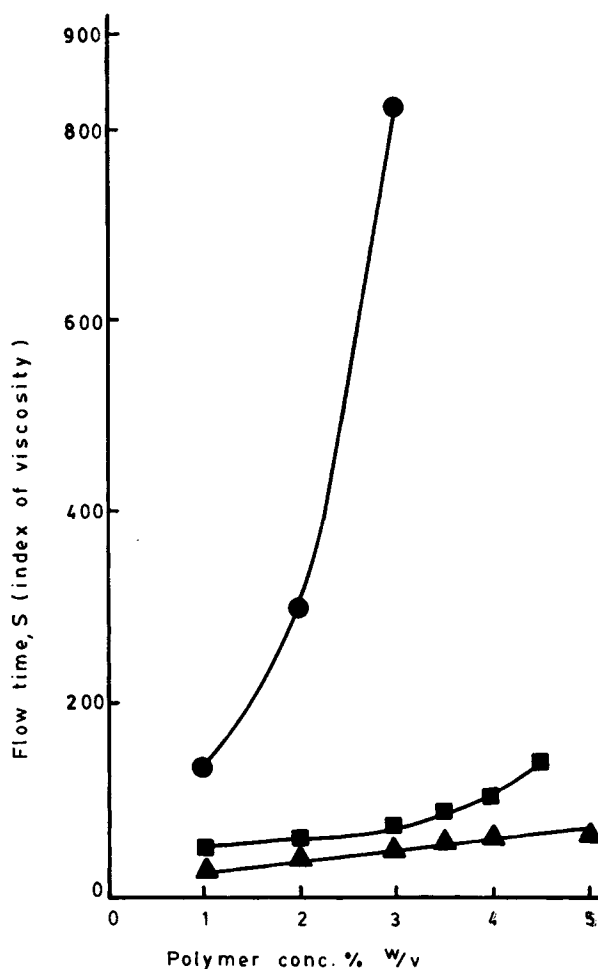
Two acrylate methacrylate copolymers designated A and B (trade names: Eudragit RL 100 and RS 100, respectively) were received from Rhom Pharma (Darmstadt, FRG). A and B differ only in their content of hydrophilic quaternary ammonium (cation) groups in a ratio 2 : 1 (A : B). Ethanol (i.e., absolute alcohol BP) was used as solvent for the polymers.

Aqueous dispersions of the polymers were formed by two methods. In the first method (coacervation) the polymer was dissolved in ethanol, and excess water (nonsolvent) was added with vigorous shaking. The amounts of ethanol used varied in different experiments (Table II). In the second method, the polymer (as fine powder) was dispersed in water at 80°C for 1 h with a Silverson mixer (Model V504) fitted with a dispersator head. Stirring was continued for another 1 h without heat. The preparation was allowed to stand 24 h and then filtered. During stirring the polymer particles deaggregated to submicroscopic sizes. Dispersion of polymer B could not be formed readily by this second method perhaps because of its lower hydrophilicity and poor hydration.

Viscosities of the liquids were measured with a U-tube (Ostwald) capillary viscometer (Model BS/U 445). Viscosity  $\eta$  is related to the time of flow by the expression

$$\frac{V}{t} = \frac{\pi Pr^4}{8\eta l}$$

where  $V$  is the volume of liquid flowing in time,  $t$  through a fine capillary of radius  $r$ , and length  $l$ .  $P$  is the liquid pressure above the capillary. For a given viscometer the terms  $V$ ,  $P$ ,  $l$ , and  $r$  are constant, and  $\eta \propto t$ . Since the present measurement was of a comparative value only, the time of flow (in seconds) of a given volume of the liquid through the capillary was taken as index of viscosity.



**Figure 1** Differences in the viscosities of HPMC solutions (●) and aqueous (coacervated) dispersions of polymers A (▲) and B (■). Note: B formed a gel at concs.  $\geq 5\%$  w/v.

Coacervated systems of the acrylatemethacrylates containing ethanol 10% v/v were used in this determination.

The minimum concentration of polymer in the dispersion which formed a gel (gel point) was determined as follows: Serial concentrations (with an increment of 0.1%  $\mu/v$ ) of the polymer in the dispersions were prepared by coacervation. Samples (10 ml) were each placed in glass test tubes and allowed to stand 24 h at room temperature,  $28 \pm 2^\circ\text{C}$ , after which they were examined for presence of gel particles. In order to study the effect of solvent on the gel point, content of ethanol in the dispersion was varied from 10 to 20% v/v. All experiments were carried out in triplicate and mean results calculated.

The results (Fig. 1) showed that in the coacervated system B, the less hydrophilic polymer with lesser cation content, formed more viscous dispersions compared with A. System A was expected to be more viscous than B based on its higher hydrophilicity and greater hydration.<sup>4</sup> The unexpected result relates to the mutual repulsiveness of the cationic groups,<sup>4</sup> which discouraged the formation of a polymeric network in the liquid structure. Thus HPMC without any cation content formed solutions that were considerably more viscous than the cationic acrylate methacrylate dispersions.

Systems of polymer A prepared by direct dispersion in hot water were about twice as viscous as the corresponding coacervated dispersions (Table I), presumably as a result of increased thermal hydration of the polymer particles.

Also ethanolic solutions of the acrylate methacrylates were about twice as viscous as their coacervated dispersions. Unlike the coacervated dispersions containing polymer-rich droplets, the organic solution is a molecular dispersion of the polymer with greater surface area for

**Table I Viscosities of Polymer A Dispersions Prepared by (a) Coacervation, (b) Stirring the Polymer in Hot Water, and (c) Dissolution in Ethanol**

Type of Dispersion	Index of Viscosity ( <i>S</i> ) of Dispersions with Polymer Conc'n (% w/v)				
	1	2	3	4	5
a	39	45	52	61	63
b	52	70	99	127	166
c	55	72	105	130	162

**Table II Effect of Solvent (Ethanol) Concentration on the Gel Point of the Coacervated Systems**

Ethanol Conc'n (% v/v)	Water Conc'n (% v/v)	Gel Point for Polymers	
		A	B
10	90	> 5 <sup>a</sup>	5
15	85	> 7.5 <sup>a</sup>	5.5
20	80	10 <sup>a</sup>	6.7

<sup>a</sup> Maximum concentration of polymer that dissolved in the given volume of ethanol.

polymer-polymer cohesive interaction, through hydrogen bonding.

The gel point was higher in A than in B (Table II), again because of the higher degree of mutual repulsiveness of the cationic charges in A. Increase in solvent (ethanol) concentration 10–20% increased the gel point only slightly.

The aqueous dispersions of the acrylate-methacrylates have the advantages of lower cost and nonflammability compared with their organic solutions. The remarkable fluidity of these dispersions compared with hydrocolloids, e.g., HPMC solutions is yet another asset which may be exploited in film coating procedures.

## References

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