Polymer Solutions from Latexes

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Synopsis

In order to characterize a polymer by its reduced viscosity, it is necessary to put it into solution. For polymer made by emulsion polymerization, this usually involves coagulating the latex, washing and drying the coagulum, and then dissolving the residue in an organic solvent. The method fails when the polymer crosslinks on drying, as is the case with some adhesive resins. The method proposed here uses mixtures of N-methylpyrrolidone (NMP) and tetrahydrofuran (THF) to put the polymer directly into solution without removing the water. The technique is applicable to many polymers and copolymers of ethyl acrylate and vinyl acetate.

INTRODUCTION

The viscosity of a latex depends very little on the molecular weight of the polymer produced. In order to follow molecular weight as a function of reaction time, the usual procedure is to coagulate the latex with a nonsolvent, dry the coagulum, and then dissolve it in an organic solvent. The last step may require hours or even days. Some reactive latexes used as binders or adhesives cannot be analyzed by this method since they crosslink on drying and become insoluble in any solvent. Freeze drying may avoid the crosslinking, but it is not always an available tool.

There are certain advantages to converting the latex to a solution without isolation of dry polymer. Essentially, the system becomes the same as a solution polymerization. Concentration still has to be established, generally by evaporation or coagulation and washing. The present work was started to find feasible systems for converting latexes of 5–50% solids directly into solutions with 0.1–1% solids. Some criteria can be used to limit the scope of the search for a system with a given polymer:

(1) The solvent system must be miscible with water.

(2) The system should be a rather good solvent for the polymer even in the absence of water.

(3) Addition of the solvent to the latex should not give a massive coagulum which is slow to dissolve. High-speed stirring should be avoided in the dissolving step in order to avoid mechanical degradation.

(4) It is desirable to operate in a solvent composition region where perturbations in solvent ratios will give little change in relative viscosity.

(5) The system should not be sensitive to changes in temperature.

(6) The solvent system itself should have a relatively low viscosity on the order of that of water or lower.

(7) The solvent system should be compatible with other systems used for polymer characterization. It may be desirable to inject the solution into a gel permeation chromatograph, for example.

CCC 0021-8995/81/051595-09$01.0

EXPERIMENTAL

Homopolymers of ethyl acrylate and vinyl acetate (Table I) were prepared by adiabatic emulsion polymerization using a recipe similar to one previously described.[1] To lower the molecular weight of some acrylate polymers, 1-dodecanethiol was added as a chain transfer agent. Three commercial latexes were also used (Table I). A portion of each polymer was coagulated by salt addition, thoroughly washed with water, and dried in an air-circulating oven at 45°C.

Polymer solutions were prepared in two ways:

(1) *Solutions from dried coagulum.* By dissolving the dried polymers in pure solvents, batches of 1% solutions in tetrahydrofuran (THF) and *N*-methyl-2-pyrrolidone (NMP) were prepared. These solutions, together with pure solvents and water, were subsequently used to prepare more dilute solutions of desired concentrations and compositions for viscosity measurements.

(2) *Solution from latex.* The solid content of the latexes was determined from the weight of the dried coagulum of a specified volume of latex solution. The latex was then diluted with water, followed by the addition of a calculated amount of NMP, and subsequently THF to give the desired concentration and composition. Some mixtures were warmed to speed up dissolution.

The viscosity-average molecular weights, M_v, of homopolymers were estimated from the following equations which apply to solutions in benzene at 30°C:

Poly(ethyl acrylate)[2]:

$$[\eta] = 2.77 \times 10^{-4} M_v^{0.67} \tag{1}$$

Poly(vinyl acetate)[3]:

$$[\eta] = 2.20 \times 10^{-4} M_v^{0.65} \tag{2}$$

While benzene was used to obtain M_v, it was not used as a component of the water-miscible systems under consideration. For all solvent systems, intrinsic viscosities were established by extrapolation to infinite dilution according to the Huggins equation[4]:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{3}$$

TABLE I
Vinyl and Acrylic Polymers

Sample identification	Intrinsic viscosity, $[\eta]$, dl/g benzene, 30°C	Molecular weight $M_v \times 10^{-5}$ eqs. (2) and (3)
Poly(ethyl acrylate)		
A	1.80	4.91
B	1.04	2.18
C	1.23	2.78
D	2.19	6.57
E	0.93	1.85
Poly(vinyl acetate)		
A′	0.91	3.68
B′	1.54	8.27
Commercial latexes		
Daratak B (W. R. Grace & Co.)		
Hycar 2600 × 84 (B. F. Goodrich Chemical Co.)		
Rhoplex HA-8 (Rohm and Haas)		

where c is in g/dl and k' is the Huggins constant obtained from the plot of η_{sp}/c vs. c.

The solvent system was derived on the basis of the following observations:

(1) Direct solution results when NMP is added to a variety of acrylate and acetate latexes. A volume of four parts NMP to one part latex is sufficient to give a viscous, hazy (in some cases), but true solution.

(2) The direct solution in NMP is rather awkward to handle and sometimes gives variable viscosities.

(3) Some common solvents for acrylate and acetate polymers which are water miscible can be used to dilute the NMP mixture without coagulation. Acetone, methoxyethanol, and THF give similar results. THF is less volatile than acetone and much less viscous than methoxyethanol. Also, THF has the advantage of being the solvent of choice in many GPC columns.

Since the regime of interest is that of 0–20 parts of water, 0–20 parts of NMP, and the balance THF, it was necessary to establish the variation in solvent viscosity with composition. In general, Heric's equation[5] gave a reasonable fit to viscosity data for the three solvent pairs. Extended to the three-component system, it was only fair. The experimental values of solvent viscosity for each composition were used in calculating η_{sp} in each case. The increase in viscosity when water or NMP is added to THF in the area of major interest is indicated in Figure 1.

RESULTS AND DISCUSSION

Poly(ethyl Acrylate)

Cloud Points

As a first step, the bounds of polymer solubility were established by titrating NMP–THF solutions to a turbid end point (cloud point) with water. Both of the higher-molecular-weight samples gave about the same result (Fig. 2). One complication is that the cloud points are hard to observe when water is added to a solution in NMP or in a mixture rich in NMP. The viscosities of high-NMP
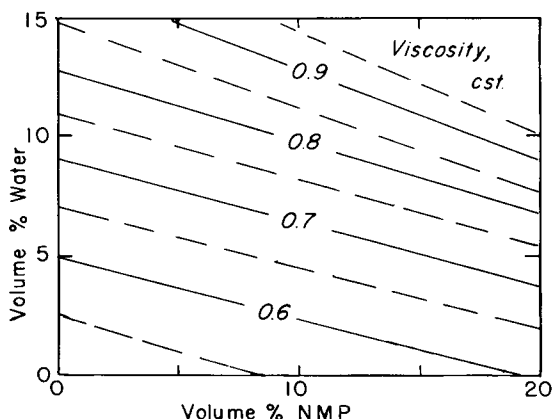

Fig. 1. Viscosity behavior of the system Water–NMP–THF in the THF–rich region. Although water is less viscous than NMP, addition of water to THF increases the viscosity (centistokes at 30°C) more than NMP at the same concentration.
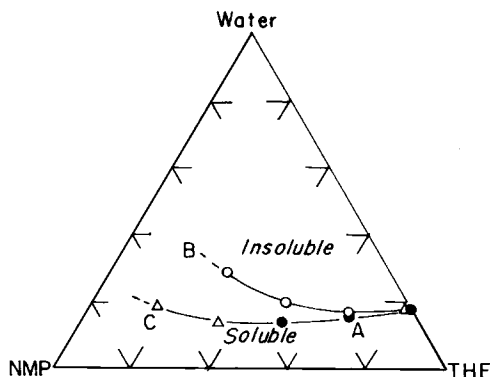
Fig. 2. Solubility boundary of 0.5 g/dl poly(ethyl acrylate) solutions. Low-molecular-weight sample B tolerates more water than samples A and C.

solutions are hard to reproduce, indicating some instability. One can speculate that the polymer separates as a highly swollen microgel phase which does not differ greatly in refractive index from the solution.

Viscosity Versus Solvent Composition

Both the kinematic viscosity and the relative viscosity for solutions of polymer A show regular behavior. With data at several concentrations, the intrinsic viscosity and Huggins constant can be derived (Fig. 3).

On the basis of intrinsic viscosity, the solvation strength of the solvents with 5% water by weight appear to be about the same as that of the solvents that contain no water.

The major purpose of the development of such a solvent is to dissolve the polymer from the latex and examine its properties. In order to prove that this method is valid, investigations were conducted to see if the solutions of a particular polymer sample prepared from the latex and from the coagulum yield similar viscosities. Intrinsic viscosity values of both kinds of solution of various samples are listed in Table II. Agreement is satisfactory.

The commercial polymer Rhoplex HA-8 is a milky-white liquid described by the manufacturer as an emulsion of self-crosslinking acrylic polymers. The dried
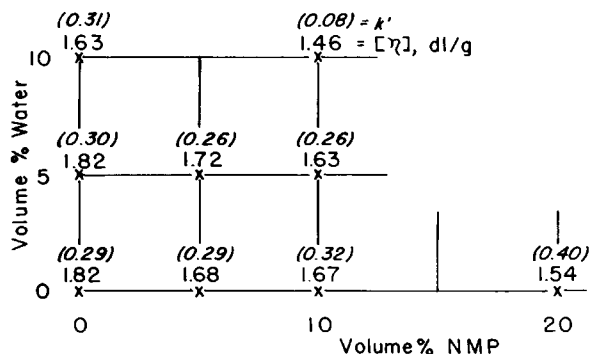

Fig. 3. Map of intrinsic viscosity and Huggins constant as a function of solvent composition for poly(ethyl acrylate) sample A.

TABLE II
Intrinsic Viscosity of Latex Solutions and Coagulum Solutions of Various Poly(ethyl Acrylate) Samples at 30°C

Sample No.	Solvent composition, vol %			Intrinsic viscosity, dl/g	
	THF	NMP	Water	Coagulum solution	Latex solution
C	90	5	5	1.11	1.08
	80	10	10	0.80	0.88
D	90	5	5	2.06	2.03
	80	10	10	1.76	1.65
E	90	5	5	0.81	0.80
	80	10	10	0.62	0.65

coagulum of this latex, which is rather tacky, swells to about three times its original size in both pure THF and NMP, but no dissolution occurs. In order to study the properties of this polymer solution, the solution must be prepared from the latex. The same kind of procedures and solvent compositions that apply satisfactorily to the homopolymer of ethyl acrylate were first applied to this latex. In contradiction to the solvation behavior of the homopolymers, where THF displays stronger solvation power than NMP, a preliminary qualitative test has shown that at approximately 10% polymer concentration, a 90% THF Rhoplex HA-8 solution remains cloudy while a 90% NMP solution is clear. This phenomenon indicates that NMP is a better solvent for Rhoplex HA-8 than THF and should be tried as the major solvent of the system. Systems high in NMP, however, give rather erratic behavior. As NMP content is reduced to 50%, the data become usable for extrapolation (Table III).

Since the composition of the latex has not been disclosed by the manufacturer, it is difficult to visualize the molecular interactions that may exist in the mixture of Rhoplex HA-8 and solvents. A specific interaction between NMP and one of the comonomers is only speculative, but the viscosity behavior observed experimentally does point in that direction.

The commercial polymer Hycar Acrylic 2600 × 84 is a milky-white latex that contains a synthetic anionic emulsifier. Similarly to Rhoplex HA-8, NMP was found to be a better solvent for this polymer than THF. A THF solution with 0.5% polymer prepared from the coagulum appears to be slightly cloudy. Nonetheless, intrinsic viscosity was determined to be 1.86 for this polymer in THF and 3.26 in NMP, both at 30°C. Despite this difference, the solvent behavior of this latex is very similar to that of the homopolymers. Intrinsic viscosities determined from the data of the solutions prepared from the latex are presented in Table IV. The variation of intrinsic viscosity shows a typical

TABLE III
Intrinsic Viscosity of Rhoplex HA-8 at Various Compositions at 30°C

Solvent composition, vol %			Intrinsic viscosity, dl/g
THF	NMP	Water	
45	50	5	0.92
50	45	5	1.23
60	35	5	0.99

TABLE IV
Intrinsic Viscosity of Hycar Acrylic 2600 × 84 Solutions at 30°C

Solvent composition, vol %			Intrinsic viscosity,
THF	NMP	Water	dl/g
95	—	5	1.61
90	—	10	1.33
90	5	5	1.64
80	15	5	1.95
75	20	5	1.82

solvation pattern of an acrylate polymer solution. The solvent strength goes down as the water content increases. The trend of higher intrinsic viscosity as the NMP content increases again indicates that NMP may be a stronger solvent than THF.

Poly(vinyl Acetate)

Cloud Points

Solubility boundaries for samples A' and B' (Fig. 4) were established. In the region of the solvent system that contains no more than 15 vol % water, complete dissolution is observed for solutions of 0.5% polymer concentration or lower. Unlike the behavior of the acrylate system, more water is tolerated in the THF-rich region than in the NMP-rich region, and a complete boundary can be constructed for the system.

Viscosity Versus Solvent Composition

Viscosity data of the coagulum solutions were used to determine the values of intrinsic viscosity of various compositions (Fig. 5). In contrast to the solvation behavior of poly(ethyl acrylate), NMP is found to be a slightly stronger solvent for poly(vinyl acetate) than THF, based on the variation of intrinsic viscosity. The criterion of Huggins constant agrees, in general, with that of the intrinsic viscosity. Deviations from the expected variation of k' with solvent power are also observed. This phenomenon is not uncommon with polar polymers, and
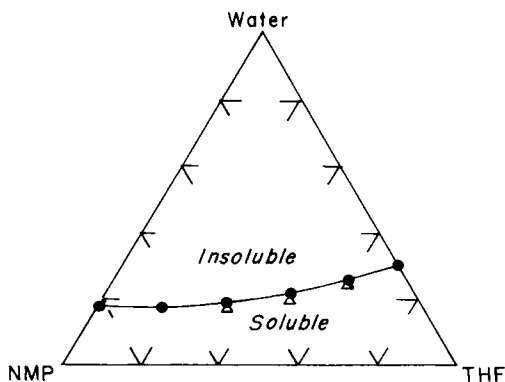

Fig. 4. Solubility boundary of 0.5 g/dl poly(vinyl acetate) solutions for samples A' (●) and B' (△).
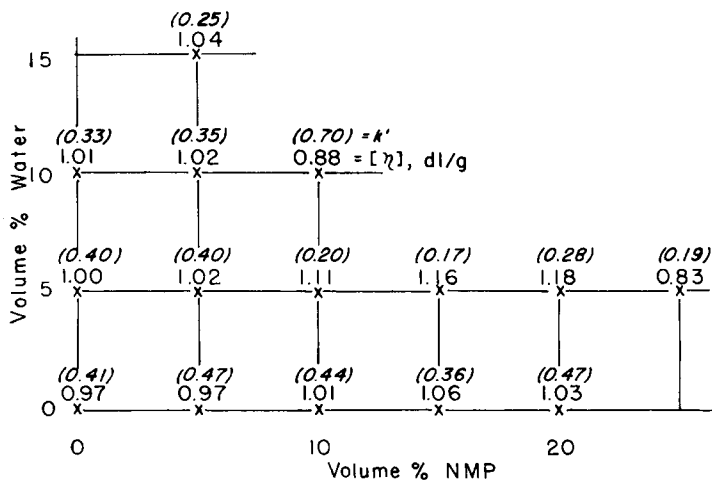
Fig. 5. Map of intrinsic viscosity and Huggins constant as a function of solvent composition for poly(vinyl acetate) sample A'.

it may be due to specific interactions between solvent and polymer.[6] Goring and Rezanowich[7] have suggested that electrical fields across the boundary between polymer and solvent may affect the values of k'. Also, with more extended and more polar polymers such as cellulose derivatives, there seems to be no apparent relationship between k' and solvent power.[8] This is the reason why the intrinsic viscosity instead of the Huggins constant is more often used as a criterion for solvent "goodness."

The viscosity data of the higher-molecular-weight sample at the solvent composition of 85% THF and 15% water display erratic behavior and are not reproducible. It is believed that even though this solution appeared to be homogeneous, it is indeed situated in the region where the water concentration is so relatively high that the long polymer chains are only partially solvated. As seen from Figure 4, this composition is located well within the solubility region previously established, so solvent compositions some distance from the boundary appear desirable. The method of preparing polymer solutions directly from the latex does not work as successfully for vinyl acetate systems as for acrylate systems. Both THF and NMP coagulate the polymer upon mixing with the latex at room temperature. These same procedures were nonetheless followed, except that NMP and the latex were heated to about 85°C before mixing. Although coagulation took place initially, the polymer rapidly started to dissolve at this temperature. The desired compositions were then prepared with the addition of THF.

Mixing the latex with a large proportion of either THF or NMP was found to be effective as well. Though coagulated, the polymer is well dispersed in either solvent and complete dissolution can be achieved in a short period of time with mild agitation. The choice of THF as the major solvent is preferred because of its rapid solvent action. Moreover, the NMP solution is more than three times as viscous as the THF solution at the same polymer concentration.

Intrinsic viscosity values determined both from the coagulum solutions and the latex solutions are listed in Table V, and very good agreement is attained. These results again substantiate an earlier conclusion that testing data of a

TABLE V
Intrinsic Viscosity of Latex Solutions and Coagulum Solutions of Two Poly(vinyl Acetate)
Samples at 30°C

Sample No.	Solvent composition, vol %			Intrinsic viscosity, dl/g	
	THF	NMP	Water	Coagulum solution	Latex solution
A′	95	—	5	1.69	1.68
	—	95	5		1.71
B′	90	—	10	1.01	1.01
	85	10	5	1.11	1.09
	80	15	5	1.16	1.17
	75	20	5	1.18	1.22

polymer solution prepared from either the coagulum or the latex are equivalent
and can be used as such. The preparation of polymer solutions directly from
the latexes is again preferred because it is a more efficient method.

Daratak B is an adhesive emulsion manufactured by W. R. Grace and is de-
scribed as an internally plasticized vinyl acetate copolymer. The solvation be-
havior of this polymer is quite different from that of the homopolymers. Like
Rhoplex HA-8, its coagulum was found to be insoluble in THF, but it appeared
to be soluble in NMP. The data indicate, however, that the viscosity behavior
of the NMP solutions is erratic and nonreproducible. It is suspected that the
behavior is caused either by strong interaction between NMP molecules and a
certain component of the latex or by the polymer being only partially dissolved
in NMP. We conclude that NMP is not a useful solvent for Daratak B for the
purpose of studying viscous flow. On the other hand, the original method was
found to be effective to prepare polymer solutions directly from the latex. In-
trinsic viscosity at various compositions was determined (Table VI). In the case
of this particular polymer, there seems to be no advantage to including NMP
at all.

CONCLUSIONS

The method proposed here uses mixtures of N-methylpyrrolidone (NMP) and
tetrahydrofuran (THF) to put the polymer directly into solution without re-
moving the water. The technique is applicable to many polymers and copoly-
mers of ethyl acrylate and vinyl acetate. The preferred water–NMP–THF
mixture should be in a region where the viscosity is not sensitive to small varia-

TABLE VI
Intrinsic Viscosity of Daratak B Solutions at 30°C

Solvent Composition, vol %			Intrinsic viscosity, dl/g
THF	NMP	Water	
90	5	5	0.70
95	—	5	1.00
90	—	10	0.76
85	10	5	0.94
80	10	10	0.67

tions in water content. Some guidelines for developing a suitable solvent system are:

(1) Add NMP or THF to the concentrated latex (20–50% solids) in a 4:1 solvent-to-water ratio at room temperature.

(2) If necessary, raise the temperature of the system.

(3) Dilute with THF to a selected concentration (usually 0.1–1.0%).

(4) Keep water in the final system below 5% for maximum stability and reproducibility.

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