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A Study of the Molecular Weight and Chain Length Distribution of Cyclocopolymers of Divinyl Ether and Maleic Anhydride

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SUMMARY

Some physical properties of a cyclocopolymer formed by an intra-intermolecular polymerization mechanism were studied. The cyclic copolymer of divinyl ether and maleic anhydride was chosen for study. Intrinsic viscosities were determined in two solvents. The weight-average molecular weight was determined by light-scattering measurements and the number-average molecular weight was determined by osmometry. Results from a sedimentation velocity pattern indicated that the chain length distribution is much broader than random, which is in agreement with the ratio of the two molecular weight determinations. The polymer was fractionated by precipitation from acetone with hexane as precipitant. Addition of sodium tetraphenyl boron was necessary to obtain separation. Correlation of intrinsic viscosity and weight-average molecular weights was not obtained because of anomalous solubility effects preventing light-scattering determinations.

INTRODUCTION

The application of an alternating intra-intermolecular mechanism of chain propagation to a large variety of systems has resulted in many different kinds of interesting high polymers containing recurring cyclic units [1]. It has been reported that 1,4-dienes and certain monoolefins copolymerize via a similar bimolecular inter-intra mechanism [2]. The kinetics of such a system are "unique" and, hence, the chain length distribution may reflect this unusual behavior. It might be expected, therefore, that these cyclo-copolymers would exhibit characteristic properties. Although there are numerous physical properties that could be examined, it was realized that these cyclopolymers possibly would not yield results markedly different from those of the well-studied binary copolymer systems. Thus, it is important to study those properties which also may yield parameters and relations that would be useful either in related cyclopolymerization studies or as additional evidence of structure.

Specifically, the study was broken down into two areas: first, a study of the chain length distribution and second, a study of molecular weight and molecular weight-viscosity relationships. Both areas of study are of interest to current polymer theory to determine if the cyclic copolymers formed by the intra-intermolecular mechanism have the characteristic "random coil" properties exhibited by other polymers. The molecular weight-viscosity relationships are important per se for the rapid characterization of products in other related cyclopolymerization studies. The bimolecular inter-intra propagating system requires special copolymerization kinetic expressions [3] and, hence, the resulting polymer might be expected to exhibit characteristic physical properties. Although the number of cyclopolymerization systems which have been studied synthetically is large, structure-property studies on the resulting copolymers generally include only required data for elucidation of the composition, e.g., degree of unsaturation, reactivity ratios, and elemental analysis [4]. Evaluation of the physical characteristics of the products has been limited to properties such as crystallizability, melting points, and density [5].

RESULTS AND DISCUSSION

Characterization of the Cyclopolymer

Chain Length Distribution. The first property studied was the chain length distribution. In radical-initiated chain polymerization systems the

chain length is determined by the time that a free radical grows before coming into contact with another such chain and couples [6]. The chain length distribution is approximated by the ratio of the weight-average molecular weight \bar{M}_w to the number-average molecular weight \bar{M}_n . In a monodisperse system these two molecular weight averages are equal.

Radical-initiated chain polymerization systems are known to form polymers in which the distribution given by \bar{M}_w/\bar{M}_n is approximately equal to 2 or lies between 1.5 and 2 if coupling is the predominant means of termination [6]. Since the termination reaction is the controlling factor in chain length distribution, it was not expected that the distribution would be appreciably different from other chain systems, since for the intra-intermolecular mechanism only the propagation step is unique [3].

Results from a sedimentation velocity pattern of a typical cyclocopolymer vs a polystyrene standard indicated that the chain length distribution is much broader than random, an estimated \bar{M}_w/\bar{M}_n of between 4 and 6 being obtained. The comparative sedimentation velocity patterns are shown in Fig. 7.

Light-Scattering Measurements

Determination of the Specific Refractive Increments of the Copolymer.

After calibration of the differential refractometer the specific refractive increment for a divinyl ether-maleic anhydride (DVE-MA) copolymer in both dimethylformamide (DMF) and acetone was determined. These results are shown in Table 1.

Turbidity Measurements of the Copolymer. After calibration of the light-scattering photometer, the absolute turbidity (τ) of the copolymer solution was determined. The transmittances of the neutral filters (F) used in determining the scattering ratio are shown in Table 2. Turbidity data for two DVE-MA copolymers are shown in Table 5, and the results are plotted in Fig. 6.

Polymer Fractionation. A stepwise continuous solvent-gradient column method similar to that developed by Flowers, Hewett, and Mullineaux [7] was attempted for fractionating the cyclocopolymer. The column used is shown in diagram in Fig. 1. However, lack of success with this method made it necessary to use a fractional precipitation method using the technique described by Flory [8].

The copolymer, dissolved in acetone, was precipitated by adding petroleum

Table 1. Specific Refractive Increment of Divinyl Ether-Maleic Anhydride Cyclocopolymer

Determination	Dimethyl formamide	Acetone
1	0.083	0.165
2	0.084	0.176
3	0.082	0.171
4	0.082	—
Av	0.083	0.171
Std deviation	0.6×10^{-3}	3.91×10^{-3}

Table 2. Transmittances of Neutral Filters

Blue light wavelength 436 m μ	
Filter	Value
F ₁	0.461
F ₂	0.235
F ₃	0.129
F ₄	0.0523

ether; however, because of an unusual inverse temperature effect (as the temperature was increased, the mixture became more turbid) this approach was abandoned. Attempts to use hexane in place of petroleum ether were also unsuccessful. However, it was found that addition of sodium tetraphenyl boron to the turbid solution of the copolymer in acetone to which hexane had been added caused an immediate flocculation and separation. This method was used to fractionate the copolymer. The viscosity data for two samples of DVE-MA copolymer in acetone are shown in Table 3. Viscosity data for a DVE-MA copolymer in DMF are shown in Table 4, and light-scattering turbidity data in Table 5.

Solubility Characteristics. Various treatments of the polymer were found to change the solubility characteristics of the samples markedly. Difficulty

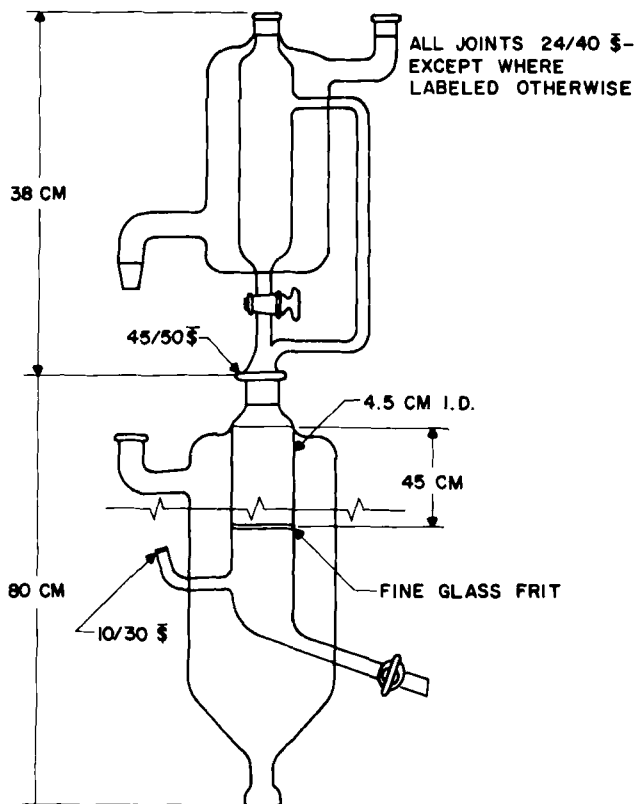


Fig. 1. Stepwise fractionation column.

was experienced in removing polymer from the glass beads taken from the column after the attempted stepwise column fractionation. The polymer seemed to adhere to the glass beads and vigorous stirring with several aliquots of acetone was required to recover the sample. This adherence to the glass beads is believed to be the reason why the column method of fractionation was unsuccessful. The solubility characteristics of fractions precipitated from acetone with hexane have not been explained. Some fractions were found to be soluble in acetone while others were found to be virtually insoluble. Stirring and vigorous shaking were found to be beneficial in obtaining solution only in some cases. As all samples were treated essentially in the same manner, there is no explanation for these solubility differences. More study is needed to determine the causes of this anomalous behavior.

Table 3. Viscosity Data of Divinyl Ether-Maleic Anhydride Cyclopolymer Samples 24 and 25 in Acetone^a

Sample	Concentration (g/dl)	Average time (sec)	η_{rel}	η_{sp}/c	$\ln \eta_{rel}/c$
Sample 24					
Acetone	(5 ml)	105.1	—	—	—
1	0.468	121.1	1.151	0.319	0.296
2	1.828	191.4	1.821	0.449	0.327
3	1.097	149.6	1.442	0.383	0.319
4	0.718	129.5	1.231	0.324	0.288
Sample 25					
Acetone	(5 ml)	105.5	—	—	—
1	1.827	156.1	1.481	0.263	0.215
2	1.096	133.4	1.262	0.237	0.211
3	0.944	127.3	1.210	0.222	0.202
4	0.567	117.3	1.111	0.194	0.184

^aTemperature, $30 \pm 0.1^\circ\text{C}$.

A calculation of the intrinsic viscosity of the first fraction was necessary because of its only slight solubility in acetone. The value was computed by use of the relationship $\sum W_i [\eta_i] = [\eta]$ [9] and resulted in an intrinsic viscosity of 0.493. A summary of fractionation results of the DVE-MA copolymer (Sample No. 24) is shown in Table 6.

The inverse temperature relationship observed in the fractionation of the copolymer from acetone-hexane has been observed in fractionation work from ketone solvents on similar maleic anhydride copolymers [10]. The effect is thought to be due to increased solvation as the temperature is decreased. The acetone breaks the intramolecular bonds, forming what corresponds to a polymer-solvent "compound" at the lower consolute temperature, an occurrence that has been observed in many nonpolymeric solute-solvent systems [11]. As the temperature is increased this "compound" is decomposed because of the increase in kinetic energy of the low molecular weight acetone. The polymer then precipitates from the acetone-hexane solution.

Table 4. Viscosity Data of Divinyl Ether-Maleic Anhydride Cyclocopolymer Sample 24 in Dimethyl Formamide^a

Sample	Concentration (g/dl)	Average time (sec)	η_{rel}	η_{sp}/c
DMF	(5 ml)	217.5	—	—
1	0.164	250.5	1.151	0.921
2	1.800	673.4	3.096	1.164
3	0.960	358.9	1.650	0.677
4	1.600	475.3	2.185	0.740
5	0.205	251.1	1.154	0.751
6	0.256	270.9	1.245	0.957
7	0.320	281.8	1.291	0.909

^aTemperature, $30 \pm 0.1^\circ\text{C}$.

Fractional Precipitation Using Sodium Tetraphenyl Boron. When hexane was added to the dilute polymer solution in acetone, prepared for fractional precipitation, a white, turbid, opaque polymer phase formed which was dispersed throughout the solution and would not flocculate and settle from the solution. Cooling to 0° would put the dispersion back in solution and slow warming to ambient temperature brought the same opaque dispersion. The desired phase should have a translucent appearance as in reality in a fractionation the system actually separates into two liquid phases [8]—one relatively rich in polymer, inaccurately termed the precipitate, and the supernatant phase. Immediately after the addition of sodium tetraphenyl boron to the system, the solution changed from opaque to translucent and the desired separation began as polymer solvent globules separated as a gelatinous mass. This addition not only caused the dispersed polymer to flocculate but it also seemed to precipitate some polymer from solution.

It is proposed that the function of sodium tetraphenyl boron in the fractionation from acetone is to change the ionic character of the acetone. The proposal is explained in the following discussion.

Acetone seems to be a "poor" solvent for the copolymer, because it does not appear to swell the polymer coil, i.e., the typical transparent gel was not observed. This is probably because it is not strong enough ionically to interact with the polar polymer molecules. The low intrinsic viscosity

Table 5. Light-Scattering Turbidity Data for Divinyl Ether-Maleic Anhydride Cyclocopolymer Samples in Dimethyl Formamide

Solution	Concentration (g/ml) (10^3)	Galvanometer readings				Filters		$\tau - \tau_{\text{solv}}$ (10^4)	Hc/ τ (10^8)
		0°	90°	45°	135°	0°	45 and 135°		
DMF									
		Sample 25							
1	6.41	7.20	9.02	9.50	10.00	1, 3, 4	1	4.25	—
2	3.84	8.00	9.81	9.05	8.00	1, 4	1	27.95	4.91
3	1.54	7.06	9.92	9.70	8.50	2, 4	1	14.65	5.60
4	0.62	6.07	9.88	5.12	4.70	3, 4	2	7.70	4.27
5	0.25	9.29	9.86	10.00	10.00	3, 4	1	3.56	3.72
		6.00	9.75	9.52	— ^a	1, 3, 4	1	1.26	4.20
		Sample 24							
1	6.32	7.67	9.85	8.95	7.87	1, 4	1	29.60	4.56
2	4.72	8.94	9.50	8.25	7.60	1, 4	1	23.65	4.28
3	2.37	8.56	9.90	8.26	7.60	1, 2, 3	1	13.35	3.80
4	1.18	6.91	9.99	7.90	9.00	3, 4	1	6.40	3.94
5	0.51	8.80	9.86	8.18	9.45	1, 2, 4	1	2.68	4.05
6	0.21	5.90	9.67	8.20	9.95	1, 3, 4	1	1.25	3.48

^aOff scale.

Table 6. Summary of Fractionation Results of Divinyl Ether-Maleic Anhydride Cyclocopolymer Sample 24

Fraction	Hexane added (ml)	Weight of fraction (g)	$[\eta]$
1	50	1.324	0.493 ^a
2	10	0.984	0.425
3	6	0.589	0.240
4	5	0.318	0.220
5	7	0.386	0.185
6	17	1.092	0.130
7	20	0.308	0.075
8	30	0.293	0.055
9	50	0.279	0.019

^aCalculated.

obtained in acetone (Fig. 3) is in agreement with it being a "poor" solvent. When the precipitating agent is added in the fractionation, the polymer comes out of solution as tightly coiled molecules and not as solvent swollen polymer coils—a probable reason for the opaqueness of the solution instead of a translucent appearance. The addition of sodium tetraphenyl boron then, presumably, gives the solvent more ionic character to such an extent that it breaks the intramolecular attractions to allow swelling to take place. As this takes place between the dispersed polymer and the polymer in solution, two distinct solvent phases appear, the solution becomes translucent, and separation is obtained.

Two other observations seem to be in agreement with the preceding explanation. Sodium tetraphenyl boron was added to a highly swollen gel in acetone of the first fraction collected. Upon addition the gel was broken and immediate solution was observed. A highly swollen gel in dimethyl formamide reacted in the same manner upon addition of the salt. It is plausible that both went into solution because of the increased ionic character of the solvent caused by the breaking the highly polar interaction of the polymer segments.

This tentative proposal seems also to be in agreement with the work of Loehr and Schultz [12] and Figini and Schultz [13] on the anionic

polymerization of polystyrene in tetrahydrofuran. Here the salt depressed the disassociation of active ends, which reduced considerably the rate of polymerization and narrowed the molecular weight distribution.

Infrared Studies

A representative IR spectrum (Fig. 2A) showed a weak absorption band at 6.1μ , indicating vinyl unsaturation. There was no apparent differences

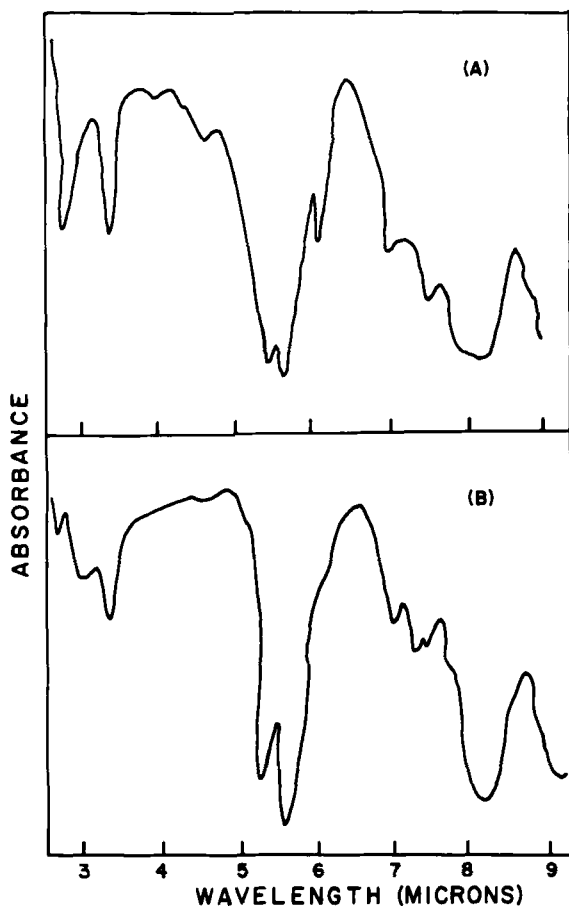


Fig. 2. Infrared spectra of divinyl ether maleic anhydride cyclocopolymer. (A): Original Sample No. 24. (B): Sample No. 24 after precipitation with Hexane.

in the IR spectrum of the insoluble sample (Sample No. 22) and the other two soluble samples (Samples Nos. 24 and 25). No changes in the IR spectra were observed by dissolving the polymer in acetone and then drying to form a film. However, samples precipitated from acetone with hexane or petroleum ether showed a marked change as the unsaturation band disappeared. This result is shown in Fig. 2B. A possible explanation for this change is that low molecular weight fractions containing the majority of the vinyl unsaturation were removed by this solution precipitation technique.

Intrinsic Viscosity and Osmotic Pressure Measurements

Intrinsic viscosity plots of DVE-MA copolymers in acetone are shown in Fig. 3. Intrinsic viscosity plots of the various fractions of the fractionated DVE-MA copolymer (Sample No. 24) in acetone are shown in Fig. 8, and the results are shown in Table 7.

Unusual slopes of the reduced viscosity vs concentration curve (Fig. 4) and the osmotic pressure vs concentration curve (Fig. 5) were obtained when these determinations were done in dimethyl formamide.

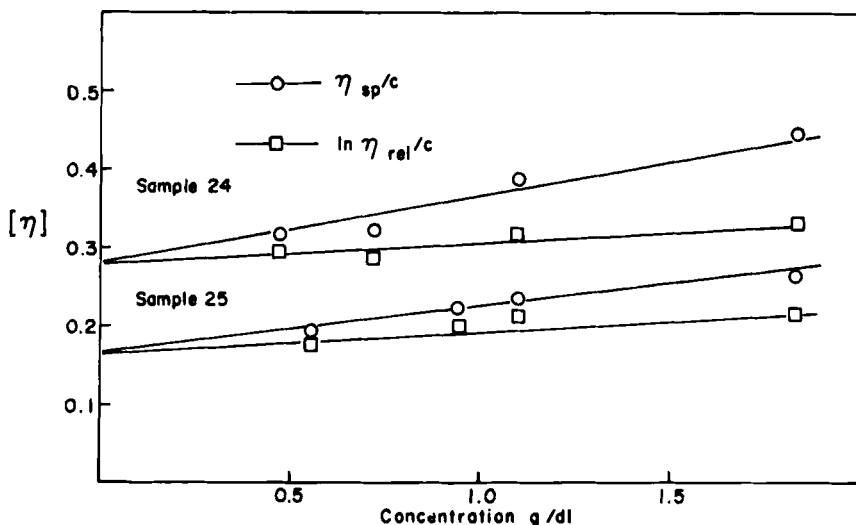


Fig. 3. Intrinsic viscosities of divinyl ether maleic anhydride cyclocopolymer Samples Nos. 24 (above) and 25 (below) in acetone at $30 \pm 0.1^\circ\text{C}$.

Table 7. Intrinsic Viscosity Results for Fractions of Divinyl Ether-Maleic Anhydride Cyclocopolymer Sample 24 in Acetone^a

Fraction	Concentration (g/dl)	Average time (sec)	η_{rel}	η_{sp}/c	$[\eta]$
1	—	—	—	—	0.493 ^b
2	1.120	157.0	1.510	0.455	
	0.896	144.6	1.395	0.443	
3	0.448	124.4	1.200	0.447	0.425
	0.738	123.3	1.190	0.258	
	0.592	119.1	1.150	0.254	0.240
	0.296	111.8	1.079	0.268	
4	0.754	123.0	1.185	0.246	0.220
	0.604	118.3	1.139	0.232	
	0.810	121.4	1.171	0.209	0.185
	0.648	117.3	1.130	0.201	
6	1.490	127.7	1.228	0.153	0.110
	1.196	122.2	1.180	0.151	
7	0.835	112.3	1.081	0.097	0.075
	0.700	110.3	1.061	0.037	
8	0.865	110.8	1.064	0.074	0.055
	0.715	109.9	1.057	0.080	
9	0.585	105.7	1.017	0.029	0.019
Acetone	(5 ml)	103.9			

^aTemperature 30 ± 0.1°C.^bCalculated.

EXPERIMENTAL

Materials and Sources (used as received unless stated otherwise). DVE-MA Copolymers (Samples Nos. 22, 24 and 25), Department of Chemistry, University of Florida; acetone (reagent grade) Fisher Scientific Co., distilled for use in fractionation and distilled and dried over molecular sieves for use in viscosity determinations; dimethyl formamide (reagent grade) Fisher

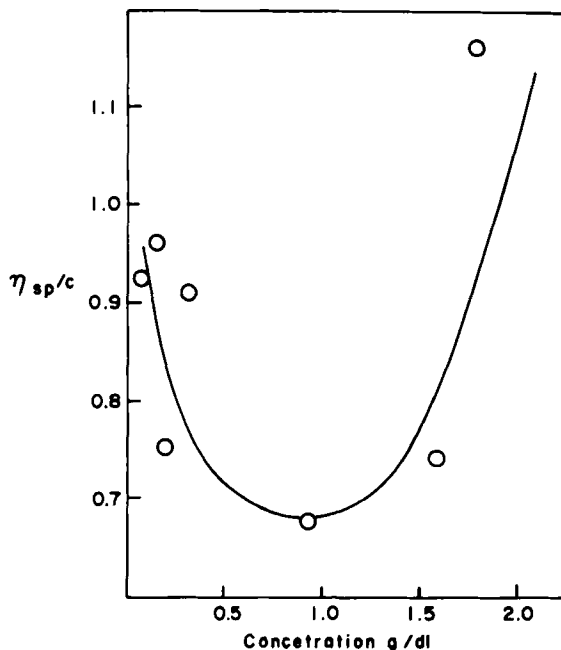


Fig. 4. Intrinsic viscosity of divinyl ether maleic anhydride cyclocopolymer Sample No. 24 in dimethyl formamide at $30^{\circ} \pm 0.1^{\circ}\text{C}$.

Scientific Co.; glass beads (number 130), Minnesota Mining and Manufacturing Co.; hexane (practical), Eastman Organic Chemicals Co.; petroleum ether (low boiling), Eastman Organic Chemicals Co.; polystyrene, obtained from Mellon Institute; potassium chloride (reagent grade), J. T. Baker Co.; sodium tetraphenyl boron (reagent grade), J. T. Baker Co.; and toluene (technical grade) distilled before use.

Equipment. Brice-Phoenix differential refractometer, on loan from the University of Florida; Cannon Ostwald capillary viscometers A-375 and A-377; Perkin-Elmer Model 137 Infracord; Thermostatic mercurial regulated water bath, E. H. Sargent and Co.; and Todd Precise Fractionation Assembly.

Polymer Fractionation

(a) **Stepwise Column Method of Fractionation.** A stepwise column method of fractionation of the cyclic copolymer was attempted in the

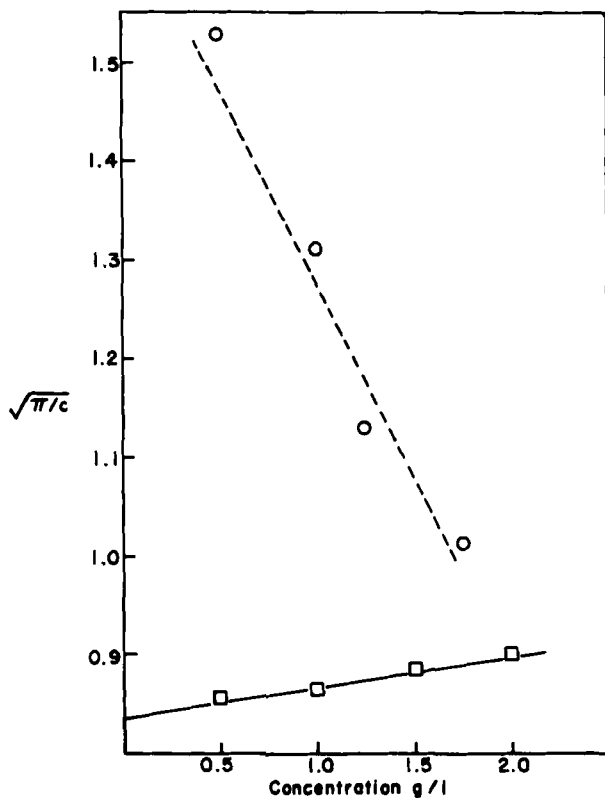


Fig. 5. Osmotic pressure results of divinyl ether maleic anhydride cycloco-polymer Sample No. 25 in dimethyl formamide (dotted curve) and in acetone (solid curve).

manner of Flowers et al. [7]. The column diagrammed in Fig. 1 was packed by filling two-thirds full with isopropyl alcohol and then slowly pouring glass beads into it with constant shaking to provide uniform packing. The isopropyl alcohol was then flushed from the column with petroleum ether. Care was taken not to let any portion of the packing become dry. Approximately 6 g (6.3245 g) of polymer were precipitated on about 200 g of the beads by evaporating an acetone solution of the polymer with stirring under a nitrogen blanket. At the point where the solvent was almost gone and the mass became viscous, petroleum ether was added to precipitate the polymer. Good coating of the beads appeared to be obtained. The polymer-coated beads were then transferred to the column which was maintained at a temperature of 0°C.

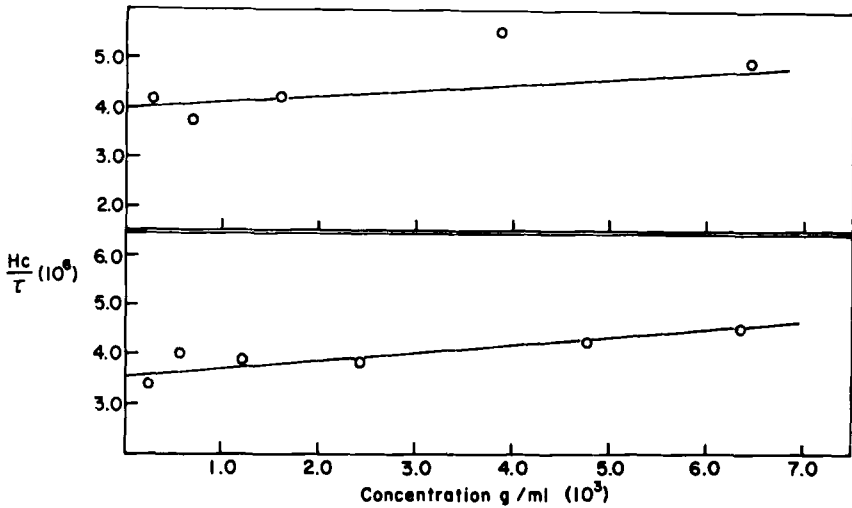


Fig. 6. Light-scattering results of divinyl ether maleic anhydride cyclocopolymer Samples Nos. 24 (below) and 25 (above) in dimethyl formamide.

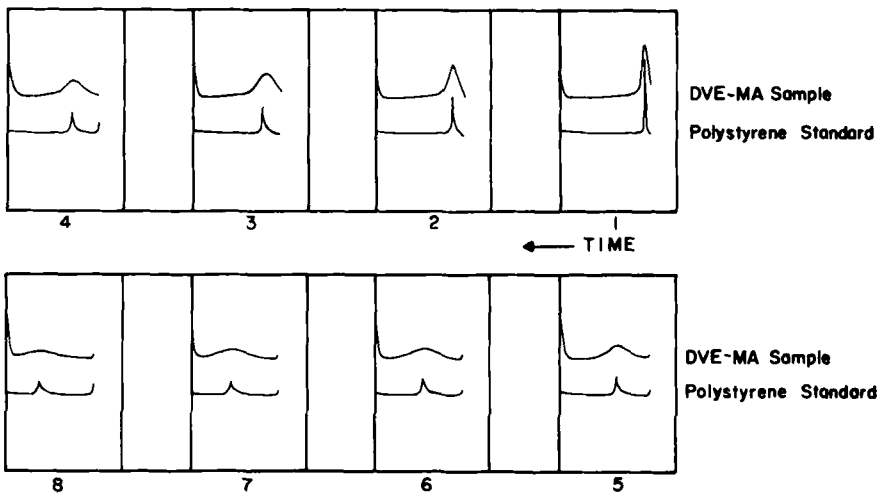


Fig. 7. Sedimentation velocity pattern of divinyl ether maleic anhydride cyclocopolymer (Sample No. 25) in acetone vs. polystyrene in cyclohexane.

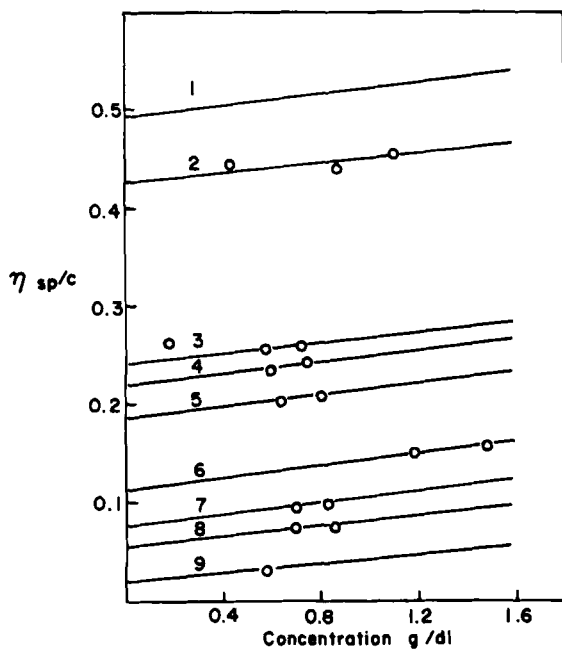


Fig. 8. Intrinsic viscosities of divinyl ether maleic anhydride cyclocopolymer Sample No. 24 fractions in acetone at $30 \pm 0.1^\circ\text{C}$. Curve 1 was calculated.

In the stepwise method of Flowers [7] the refractive index was measured to determine when one composition had eluted all of its fraction. For the polymer-solvent system used in this study, this measurement was impractical; therefore to approximate the stepwise characteristic of the fractionation, the holdup of the column was determined. Specific volumes of the different compositions were added and fractions were collected which were equal in volume to that of the respective eluent. The eluent composition was varied from 12% acetone in hexane to pure acetone in twelve steps, each increment being 200 ml in volume. Even the pure acetone failed to elute appreciable polymer and, indeed, the swollen polymer clogged the frit and prevented further solvent flow. This same technique was attempted at a column temperature of 36.5° with comparable results.

(b) Fractional Precipitation Method. Since the column elution method was unsuccessful, a fractional precipitation was attempted using the technique described by Flory [8]. Approximately 4 g (4.0614 g) of polymer

was dissolved in 500 ml of acetone, placed in a large fractionation flask at 0°, and petroleum ether added until a slight turbidity persisted. On warming to obtain homogeneity, however, an inverse temperature effect was noted, i.e., as the temperature was increased, the mixture became more turbid. The planned approach of carrying out fractionation at 0° was abandoned, and fractionation was attempted at 30°. A turbid mixture was cooled to 0° until homogeneous and then warmed slowly with stirring to 30° and left for 24 hr. No separation was observed as the precipitated layer remained dispersed throughout the solution.

Two other attempts were made to fractionally precipitate the polymer from acetone. In the first, hexane was used in place of petroleum ether as the precipitating agent and in the second, dried and distilled acetone was used to eliminate water as a factor. Both attempts were unsuccessful because the polymer would not form the desirable viscous, polymer-rich liquid phase.

Attempts at centrifugation and filtration of the solution were unsuccessful. Several salts, which were insoluble in acetone, were added to the solution and had no effect, i.e., sodium chloride, potassium chloride, sodium acetate, ammonium acetate, and calcium acetate. Sodium tetraphenyl boron, when added to a turbid solution of polymer, caused an immediate flocculation and separation. Studies were made on a trial fractionation to determine whether the precipitated polymer was chemically changed and whether this addition caused a selective precipitation. Results were such that sodium tetraphenyl boron was used in the following fractional precipitation procedure.

Acetone (500 ml), distilled in the Todd Still and dried over molecular sieves for 24 hr, was poured into a 1-liter ground glass round-bottom flask. Sodium tetraphenyl boron (0.5 g) was added to the acetone. DVE-MA copolymer (5.3283 g) was added to the solution. The solution was shaken occasionally until the polymer was completely dissolved. Hexane was added at room temperature until turbidity persisted in the solution. The flask was then stoppered and placed in a cold bath at 0° until the solution had cleared, about 1 hr being required. After warming slowly to ambient temperature, the flask was placed in a 30.0° bath. Approximately 6 hr was required for the fraction to completely separate as a thick gelatinous mass in the bottom of the flask. The supernatant liquid was decanted and more hexane added; the process was then repeated. Each fraction was dissolved in acetone and the sample recovered by evaporation of the solvent in tared aluminum cups.

Light-Scattering Measurements

Determination of the Specific Refractive Increment. The differential refractometer was calibrated as described in the instrument manual [14] by use of a distilled water solution of KCl that had been dried in vacuo at 90° for 3 hr. Two standard solutions were prepared. Solution 1 contained 0.2799 g of KCl in 100 ml of distilled water, and Solution 2 contained 1.4911 g of KCl in 100 ml of distilled water. Measurements were first recorded with distilled water in both compartments of the cell to determine the solvent zero reading and then with the calibration standard in the sample compartment against water in the reference compartment.

In determinations for the polymer-solvent system the solvent zero reading was determined for the solvent, either acetone or dimethyl formamide. Readings were then made by using various polymer concentrations in the sample compartment against the solvent in the reference cell. The compartments were thoroughly rinsed with solvent before and after use. A hypodermic syringe was used to remove solutions and solvents from the compartments.

The results for the specific refractive increments for DVE-MA copolymer in both dimethyl formamide and acetone are shown in Table 1.

Clarification of Solutions. Solution clarification, i.e., removal of dust and all other extraneous particles, has been emphasized throughout the literature in all light-scattering techniques. This was accomplished by filtering the solutions with nitrogen pressure through an ultrafine glass frit directly into the cell used for the turbidity measurement. This cell was removed from the filtration apparatus and the clarity was checked by placing the cell in front of the telescope of the differential refractometer. Dust particles showed up as points of light through the telescope when the cell was illuminated with light from an outside source. Differences were observed in unfiltered solutions and filtered solutions by this method.

Turbidity Measurements of the Polymer. As recommended by Stacey [15] and by Carpenter and Krigbaum [16], the instrument was calibrated with a sample of known weight-average molecular weight. This calibration using polystyrene ($\bar{M}_w = 1.6 \times 10^5$) was made in toluene. The specific refractive increment is 0.123 for this system [17]. Solutions were filtered once as described earlier and then placed directly into the instrument for measurement. All measurements were made with blue light (436 m μ). Readings were taken at 0, 45, 90, and 135° according to the procedure

outlined in the instrument manual [18]. A straight-line relationship was obtained upon plotting H_c/τ vs concentration.

A series of concentrations was run by removing the sample from the instrument after readings were taken on the original solution, taking the desired aliquot with a pipet, and diluting to volume in a volumetric flask with solvent. The resulting solution was then filtered before measuring. This technique was used for the polystyrene calibration and dimethyl formamide DVE-MA determinations. For determinations in acetone a filtered stock solution of acetone was prepared and samples were diluted directly in the light-scattering cell.

The absolute turbidity (τ) of a solution measured in the light-scattering photometer is

$$\tau = 1.14n^2(R_w/R_c[aF(G_s/G_w)])$$

where G_s/G_w is the scattering ratio or averaged observed ratio of the galvanometer deflection for the light scattered from the solution at 90° to that for the transmitted light at the 0° position. The product of the transmittances of the neutral filters used in determining the scattering ratio is F as shown in Table 2. In the equation, a is an instrument constant and R_w/R_c is an experimentally determined factor for incomplete compensation of refraction effects which, for cells of size smaller than 30×30 mm, is negligible, as was the case in this study.

The molecular weight is then determined by means of the Debye equation [19] where $H = 15.2 \times 10^{-5} n^2(dn/dc)^2$. Although the squared term, n , is the refractive index of the solution, it is replaced in dilute solution by the refractive index of the solvent.

If the particles in solution are larger than about one-tenth of the wavelength of the light, scattering will not be symmetrical about 90° , i.e., the scattering will be greater along the incident light beam. A measure of this dissymmetry of scattering is made by taking the ratio of the scattering at 45 to 135° . To get accurate dissymmetry measurements requires almost absolute clarity of solutions. A perfectly clarified solvent would have a dissymmetry of unity. Measurements were made at 45 and 135° , but solution clarity and a slight misalignment of the instrument invalidates these measurements.

The results of the light-scattering turbidity measurements in DMF for DVE-MA copolymer Samples Nos. 24 and 25 are shown in Table 5.

Intrinsic Viscosity Measurements. Solution flow times were measured

in both acetone and dimethyl formamide using a Cannon-Oswald viscometer (type A-375) in a water bath at $30 \pm 0.1^\circ$. The kinetic energy correction for this viscometer was negligible because the flow time of the solvent was greater than 100 sec.

The intrinsic viscosity of a solution was taken as the intercept of the reduced viscosity (η_{sp}/c) and of the inherent viscosity ($\ln \eta_{rel}/c$) when extrapolated to zero concentration. The specific and relative viscosity η_{sp} and η_{rel} are defined by the relations

$$\eta_{sp} = (t - t_s)/t_s$$

and

$$\eta_{rel} = t/t_s$$

where t is the solution efflux time and t_s is the solvent efflux time. The solution concentration (c) is expressed in grams per deciliter.

Characterization of Unfractionated Samples. IR spectra of the three DVE-MA copolymer samples, generously supplied by Dr. G. B. Butler and Ken Joyce of the University of Florida, were the same as shown in Fig. 2. Sample Nos. 24 and 25 were soluble in acetone and dimethyl sulfoxide along with the previously known solvent dimethyl formamide. Sample 22 formed a swollen gel in these solvents, suggesting that it was crosslinked.

The intrinsic viscosities of Sample Nos. 24 and 25 in acetone were 0.280 and 0.165, respectively, as shown in Fig. 3 and Table 3. An intrinsic viscosity of Sample No. 24 in dimethyl formamide resulted in a nonlinear curve of inherent viscosity vs concentration as shown in Fig. 4 and Table 4.

Osmotic pressure was measured on Sample No. 25 in both acetone and dimethyl formamide. The measurements were made on a Mechrolab High Speed Membrane Osmometer [17]. A number-average molecular weight of 47,500 resulted from the measurement in acetone. The number-average molecular weight was not calculated from the measurement in dimethyl formamide because of the negative slope of the $\sqrt{\pi/c}$ vs concentration curve as shown in Fig. 5.

A sedimentation velocity pattern [17] of Sample No. 25 in acetone vs a polystyrene standard ($\bar{M}_w = 1.8 \times 10^5$) in cyclohexane resulted in an estimated \bar{M}_w/\bar{M}_n of between 4 and 6 with quite a lot of high molecular weight species present. This estimation is made by comparing the breadth of the DVE-MA sample, the top curve in Fig. 7, to the polystyrene standard of known distribution, the bottom curve. In the sedimentation, the high molecular weight particles settle first followed by those of next highest

molecular weight, etc. This difference in sedimentation rates gives a varying refractive index of the solution which is detected and shown in the pictures.

Weight-average molecular weights were calculated from the light-scattering data, measured in dimethyl formamide, and shown in Table 3 for the unfractionated samples. A weight-average molecular weight of $250,000 \pm 25,000$ was obtained for Sample No. 25 and a value of $300,00 \pm 30,000$ for Sample No. 24. These results are shown in Fig. 6.

Fractionation Results. The results of the fractional precipitation using sodium tetraphenylboron are listed in Table 6. Primary data for intrinsic viscosities of each fraction are shown in Table 7. Molecular weights from light-scattering measurements were not calculated because the polymer precipitated on dilution.

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