

# Characterization of Copolymers Fractionated Using Supercritical Fluids

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## Synopsis

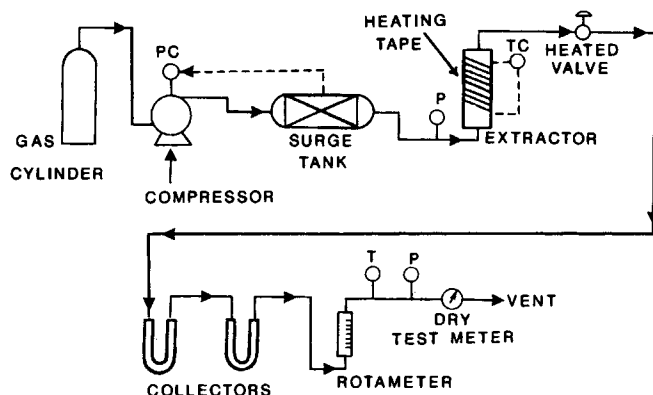
In this study supercritical fluids were used to process several different types of oligomers. Supercritical fluid processing was found to be quite effective at removing low vapor pressure monomers from polymers and for fractionation of polymers according to molecular weight. This resulted in high purity materials with low  $\bar{M}_w/\bar{M}_n$  ratios. The polymer fractions obtained were analyzed by size exclusion chromatography, differential scanning calorimetry, and melt rheometry. Their physical and chemical properties are described.

## INTRODUCTION

Supercritical fluid processing has recently received widespread attention as a processing tool in the chemical, pharmaceutical, and food industries. Use of this technology can result in lower energy costs and production of high purity materials, and is particularly attractive for processing synthetic polymers which often cannot be purified by conventional techniques such as distillation, precipitation, or filtration.

The unique solvating properties of supercritical fluids were first reported by Hanney and Hogarth<sup>1</sup> over 100 years ago. However, it was not until 1955 that Todd and Elgin<sup>2</sup> described the potential of this technology for use as a separation process. Since that time considerable effort, primarily in Germany, the United States, and the Soviet Union, has been spent to refine supercritical fluid (SCF) processing for commercial applications.

A supercritical fluid is a highly compressed gas raised above its critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ). Above the  $T_c$  and  $P_c$  the SCF can exhibit greatly enhanced solubility of a variety of solutes. Since solubility is highly dependent on the density of the fluid, small changes in temperature and pressure can be used to change its density, thus altering the solubility of the solute. By choosing an appropriate SCF and carefully manipulating temperature and pressure, selective extraction and fractionation of multicomponent mixtures can be performed. Since many synthetic polymers exist as homologous series with a distribution of chain lengths, SCFs can be used effectively to fractionate these materials according to molecular weight. Krukoniš et al.<sup>3-5</sup> have recently reported methods used to purify and fractionate synthetic polymers using SCF solvents. This paper describes the physical and chemical properties of several different types of synthetic oligomers fractionated using these techniques.



TC : TEMPERATURE CONTROLLER    PC : PRESSURE CONTROLLER

T : THERMOCOUPLE                    P : PRESSURE GAUGE

Fig. 1. Schematic diagram of supercritical fluid extractor.

## EXPERIMENTAL

Oligomer 1, a C30 + alpha olefin/maleic anhydride copolymer, was synthesized by bulk polymerization using ditertiary butyl peroxide (DTBP) as the initiator. Oligomers 2 and 3 were synthesized by solution polymerization at elevated temperature also using DTBP as the initiator. Oligomer 2 was composed of 15 mol % styrenic and 85 mol % acrylic monomers. Oligomer 3 was composed of 22 mol % styrenic and 78 mol % acrylic monomers. After synthesis, oligomers 2 and 3 were passed through a thin-film evaporator to remove solvent and unreacted monomer.

The supercritical fluid used for fractionating oligomer 1 was natural-grade propane. Oligomers 2 and 3 were fractionated using chemically pure grade *n*-butane, used as received from Matheson Gas Co.

Figure 1 is a schematic diagram of the SCF extraction apparatus. Supercritical separations were performed by charging polymer to the extractor vessel, typically a 1- or 2-in. stainless steel tube, 12 in. long fitted with a check valve at the bottom. After being filled, the vessel was connected to a high pressure system. Gas from a cylinder was supplied to the suction side of a double-end, diaphragm compressor (Superpressure, Inc.) and was compressed to the desired pressure. The system used is capable of operating at pressure levels up to 11,000 psi (750 atm). The pressure of the gas pumped to the extractor was controlled by a back pressure regulator (Circle Seal, BPR). The high pressure gas was heated to the desired temperature, typically 20–50°C above its critical temperature. The supercritical fluid, at a fixed temperature and pressure, was then pumped continuously through the extractor to partially dissolve the polymer. A stepwise increase in pressure was used to fractionate polymer according to molecular weight. Each solution of oligomer in the SCF was passed through a heated, flow-control, pressure let-down valve and expanded to ambient pressure. Precipitated polymer was trapped in two 200-mm length U-tubes connected in series. The diameter of the U-tubes was 20 mm. The expanded gas leaving the collection system was then passed

through a rotameter for flow rate measurements and through a Dry Test Meter (American Meter Corp.) for flow volume integration.

After SCF processing, each fraction was analyzed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and cone and plate viscometry. GPC analysis was performed at 35°C on a Waters 150C Chromatograph using 5  $\mu$  Styragel columns ( $1 \times 10^5$ ,  $1 \times 10^4$ ,  $1 \times 10^3$ , 500, 100 Å pore sizes) and tetrahydrofuran as the solvent. The flow rate was 1 mL/min and 200  $\mu$ L of a 0.2% solution was injected. Columns were calibrated using polystyrene standards (Polysciences Inc.). The UV detector used was a Perkin-Elmer LC 85 operated at 254 nm and 0.16 absorbance units full scale. The RI detector was the standard unit installed on the Waters chromatograph. Data were acquired on an IBM 9000 computer and were transferred to a Digital VAX 785 computer for graphical analysis using RS1 software.

Thermal analyses were performed using a DuPont Instrument 1090B/910 DSC. Instrument temperature readings were calibrated using the melt points of high purity water and indium. Samples weighing from 4 to 7 mg were held in crimped aluminum sample pans. The glass transition temperature ( $T_g$ ) was defined as the temperature at the midpoint of the overall change in heat capacity associated with  $T_g$ .

Shear viscosities of the fractions were measured using an ICI cone-and-plate viscometer. The instrument was equipped with a 0.5-in. diameter plate and a 2.0° cone. The effective shear rate was calculated as 3000  $s^{-1}$ . The accessible temperature range of the instrument was 25–200°C.

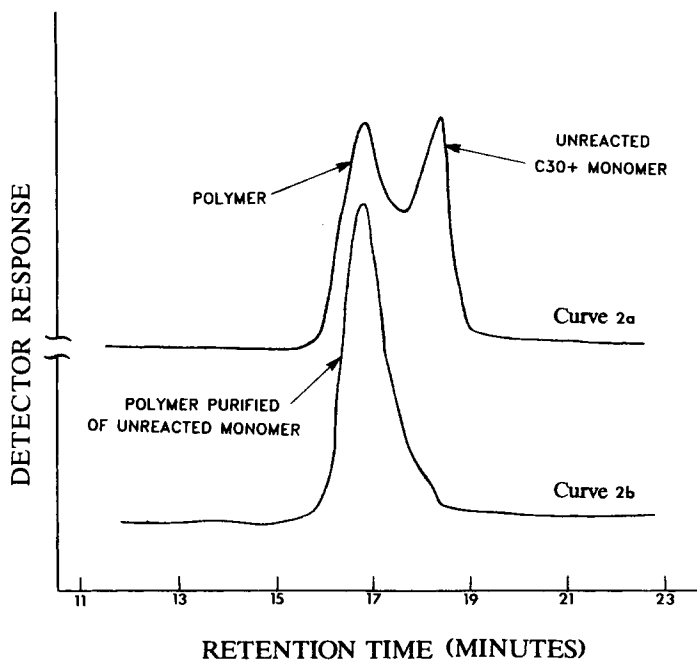


Fig. 2. Gel permeation chromatography traces of C30 + alpha olefin/maleic anhydride copolymer before and after SCF processing.

## RESULTS AND DISCUSSION

The effectiveness of SCF processing for removal of unreacted monomers from polymers is demonstrated in Figure 2. Curve 2a shows a GPC trace of oligomer 1, a bulk polymer containing a large quantity of unreacted C30 + alpha olefin monomer. Due to the low vapor pressure of this monomer, it was extremely difficult to remove by distillation or thin-film evaporation. However, SCF processing of this material produced polymer fractions which were found to be free of unreacted monomer (e.g., see curve 2b).

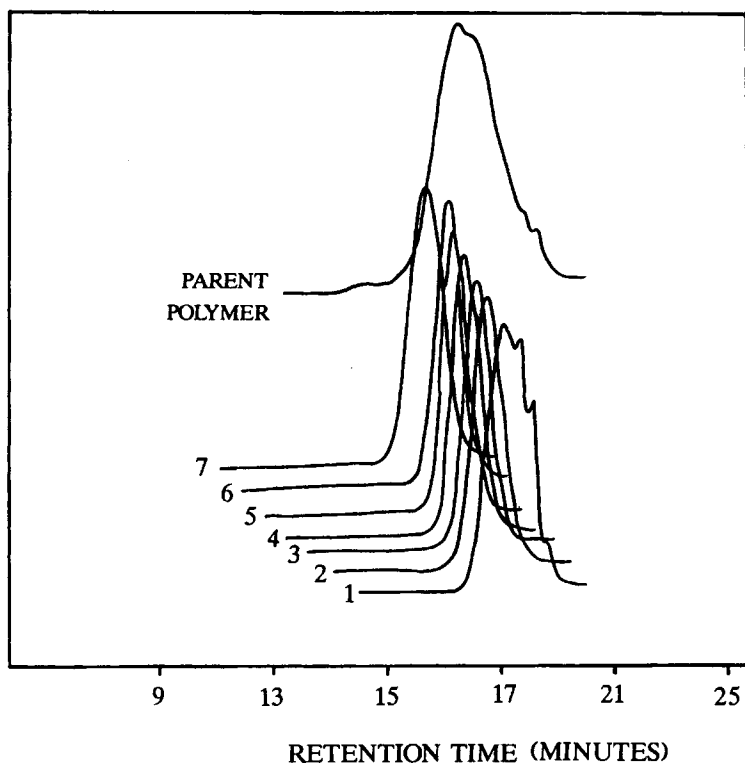


Fig. 3. Gel permeation chromatography traces of seven fractions obtained by SCF processing of oligomer 2.

TABLE I  
Molecular Weight Data Obtained after Fractionation of Oligomer 2

Fraction	Physical appearance	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_n$
1	Sticky liquid	820	860	920	1.05	1.12
2	Sticky liquid	1110	1210	1320	1.08	1.18
3	Sticky liquid	1370	1490	1640	1.08	1.19
4	Sticky solid	1740	1910	2110	1.10	1.21
5	Sticky solid	2240	2480	2730	1.10	1.21
6	Hard solid	2750	3060	3390	1.11	1.23
7	Hard solid	4910	6540	8970	1.33	1.82
Parent Material	Sticky liquid	1550	2590	5290	1.67	3.41

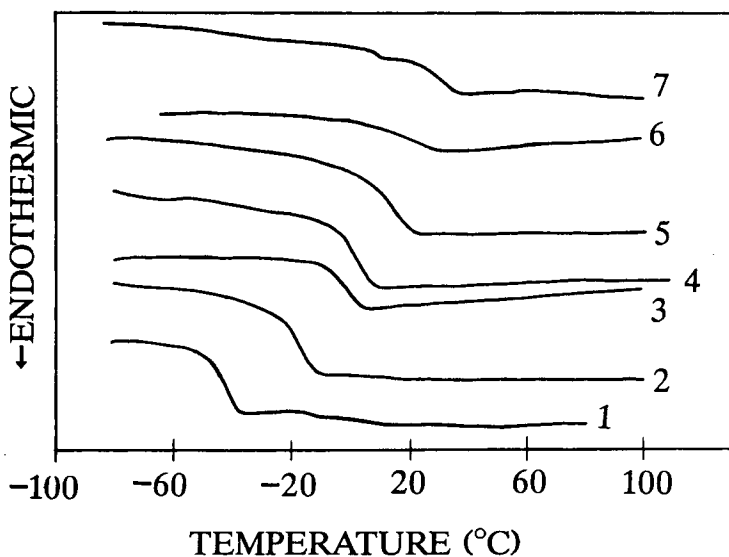


Fig. 4(a). Differential scanning calorimetry traces of the seven fractions obtained for oligomer 2.

Figure 3 shows the GPC traces of fractions obtained by SCF processing oligomer 2 along with a GPC trace of the parent material. Table I lists the physical appearance of the fractions which varied between sticky liquids and hard solids. The fractions exhibited  $\bar{M}_n$  values ranging between 820 and 4910,  $\bar{M}_w$  values between 860 and 6540, and polydispersity ratios ranging between

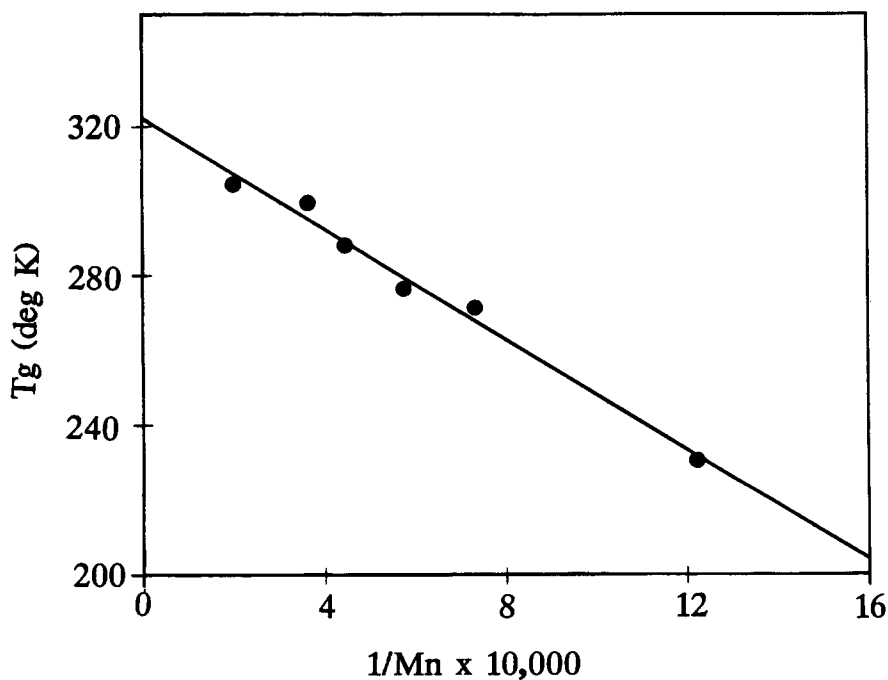


Fig. 4(b). Glass transition temperature plotted vs.  $1/\bar{M}_n$  for oligomer 2 fractions.

1.05 and 1.33 as compared to the parent material which had an  $\bar{M}_n = 1550$ ,  $\bar{M}_w = 2590$ , and  $\bar{M}_w/\bar{M}_n = 1.67$ .

Figure 4(a) shows a series of DSC traces obtained for the oligomer 2 fractions. The sharp glass transition temperatures observed ranged between  $-40$  and  $35^\circ\text{C}$ . Figure 4(b) shows  $T_g$  plotted as a function of  $1/\bar{M}_n$  for each fraction. The data are fit by the relation:  $T_g = T_g(\text{inf}) - K/\bar{M}_n$  for which a linear least-squares fit yielded  $K = 1.12 \times 10^5$  and  $T_g(\text{inf}) = 339^\circ\text{K}$ .  $T_g(\text{inf})$  represents the  $T_g$  at limiting (high) molecular weight (MW). From the theory of free volume,<sup>6</sup>  $K$  is given by  $K = 2\rho N_a \Theta / \alpha_f$ , where  $\rho$  is the density,  $N_a$  is Avogadro's number,  $\Theta$  is the fractional free volume per chain, and  $\alpha_f$  is the coefficient of expansion of free volume. In general,  $K$  is a function of endgroup composition and is on the order of  $10^5$ . For example, a  $K$  value of  $1.0 \times 10^5$  has been reported for fractions of polystyrene prepared by free radical polymerization.<sup>7</sup>

Figure 5(a) shows the melt viscosity  $\eta$  as a function of temperature for the six fractions of oligomer 2 along with that obtained for the parent material. The data, plotted as  $\log \eta$  (in poise) vs.  $1/T$ , suggest an Arrhenius relation of the form  $\eta = A \exp(-E_a/RT)$ , where the apparent activation energy  $E_a$  is essentially independent of MW. This is evidenced by the nearly equal slopes of the lines in Figure 5(a). Figure 5(b) shows a plot of  $\log \eta$  vs.  $\log M$  for the same fractions, with the data reduced to a constant temperature of  $139^\circ\text{C}$ . The data are plotted in terms of both  $\bar{M}_n$  and  $\bar{M}_w$  of the fractions.

The behavior is notable in two ways. First, the sensitivity of  $\eta$  to  $M$  is larger than predicted by the Rouse theory,<sup>8</sup> which predicts  $\eta \propto M$ . Secondly, the viscosity of the parent oligomer correlates more closely with the fractions in terms of its  $\bar{M}_n$  than its  $\bar{M}_w$ . This is further evidence that end-group effects are influencing viscosity at these low molecular weights.

Figure 6 shows GPC traces of these fractions obtained after SCF processing of oligomer 3, along with a trace of the parent material. Table II lists the physical appearance of the fractions which ranged from sticky liquids to white powdery solids, and the corresponding MW values.  $\bar{M}_n$  values ranged between 1400 and 18,900,  $\bar{M}_w$  values ranged between 2970 and 30,600, and yielded  $\bar{M}_w/\bar{M}_n$  ratios varying between 1.36 and 2.11 as compared to the parent material which exhibited an  $\bar{M}_n$  of 7,930,  $\bar{M}_w$  of 18,400, and  $\bar{M}_w/\bar{M}_n$  of 2.31.

The GPC analyses in Figure 6 were performed using UV and RI detectors in series where the UV detector was set at the absorption maximum for styrene. The RI detector can be considered a function of the concentration of polymer eluting from the column at a given time. The UV response is proportional to the concentration of the chromophoric group giving rise to absorbance at 254 nm as the material elutes from the column. By obtaining the ratio of UV to RI responses, a plot of the concentration of chromophore in the polymer as a function of MW is obtained. Ratios were calculated using UV and RI peak maxima obtained for each GPC run. It can be seen that the highest UV/RI response would occur in the lower MW fractions [Figs. 6(b) and (c)], which also contain two pronounced UV-absorbing peaks. As the MW increases in fractions 4, 5, and 6 [Figs. 6(d), (e), and (f)] the UV/RI response decreases, indicating a decrease in styrene level at higher MW. These fractions also lack the peaks present in the parent and low MW fractions. Figure 7(a) shows a plot of the UV/RI ratio obtained from the peak maximum for each fraction of

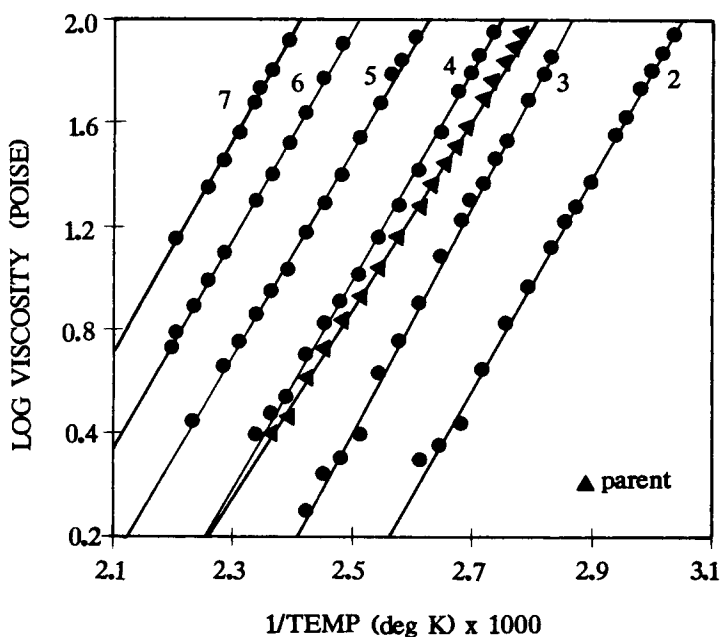


Fig. 5(a). Log viscosity (P) vs. 1/temp (K) for oligomer 2 fractions.

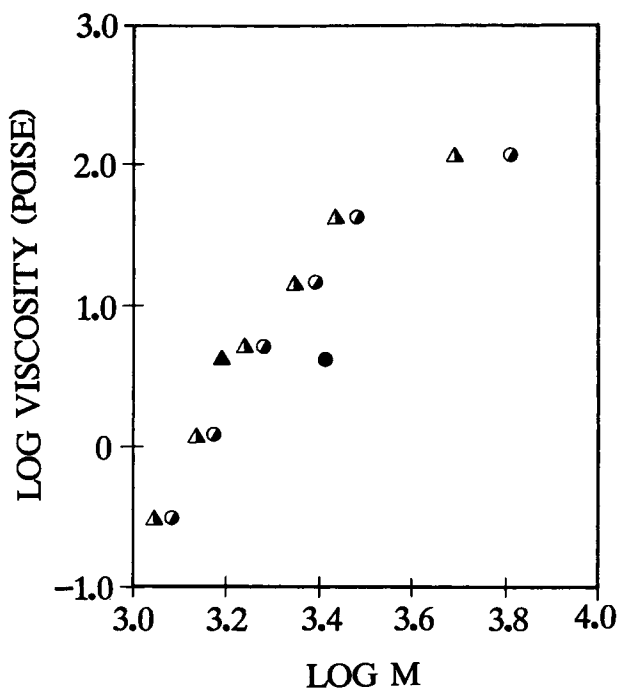


Fig. 5(b). Log viscosity (P) vs. log  $M$  for oligomer 2 fractions: ( $\Delta$ )  $M_n$  of fractions; ( $\circ$ )  $M_w$  of fractions; ( $\blacktriangle$ )  $M_n$  of parent; ( $\bullet$ )  $M_w$  of parent.

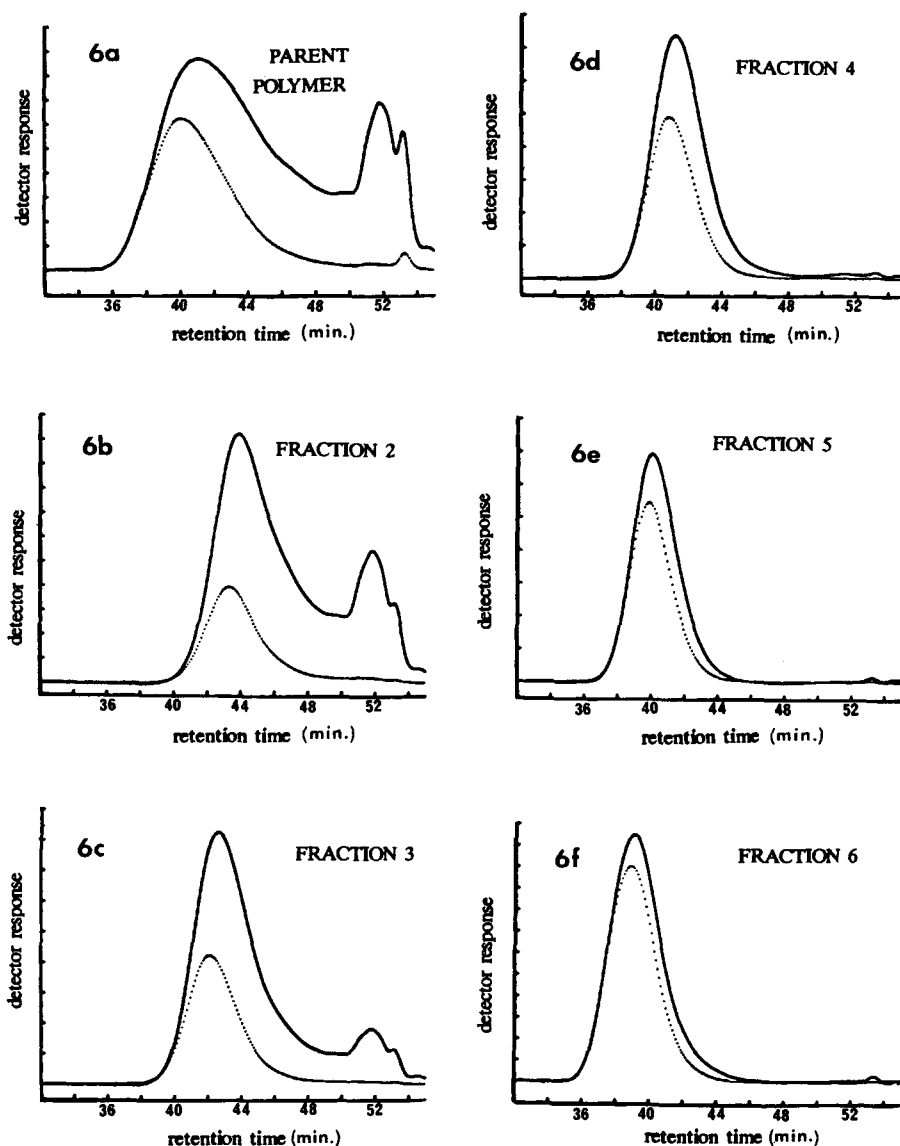


Fig. 6. Gel permeation chromatography traces of oligomer 3 obtained using simultaneous ultraviolet and refractive index detectors: (—) UV response; (···) RI response.

oligomer 3 as a function of the weight-average molecular weight. Figure 7(b) shows a similar plot made using peak maxima data obtained by simultaneous UV/RI detection during GPC analysis of oligomer 2. This data exhibits a good deal more scatter than that in Figure 7(a); however, the general trend indicates a decrease in styrene level with increased molecular weight. In Figures 7(a) and (b) the UV/RI ratios of each unfractionated, parent material has been plotted for comparison.

The trend observed in these fractions is attributed to the high temperature polymerization process used to prepare oligomers of this type, which favors



TABLE II  
Molecular Weight Data Obtained after Fractionation of Oligomer 3

Fraction	Physical appearance	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_n$
1	Very sticky solid	1400	2970	5600	2.11	3.99
2	Sticky solid	2150	4280	6490	1.99	3.02
3	Sticky solid	5770	7920	10700	1.37	1.85
4	Powdery solid	8490	12400	17500	1.46	2.06
5	Powdery solid	14200	19400	25400	1.36	1.78
6	Powdery solid	18900	30600	43000	1.61	2.27
Parent polymer	Clear solid	7930	18400	33800	2.31	4.26

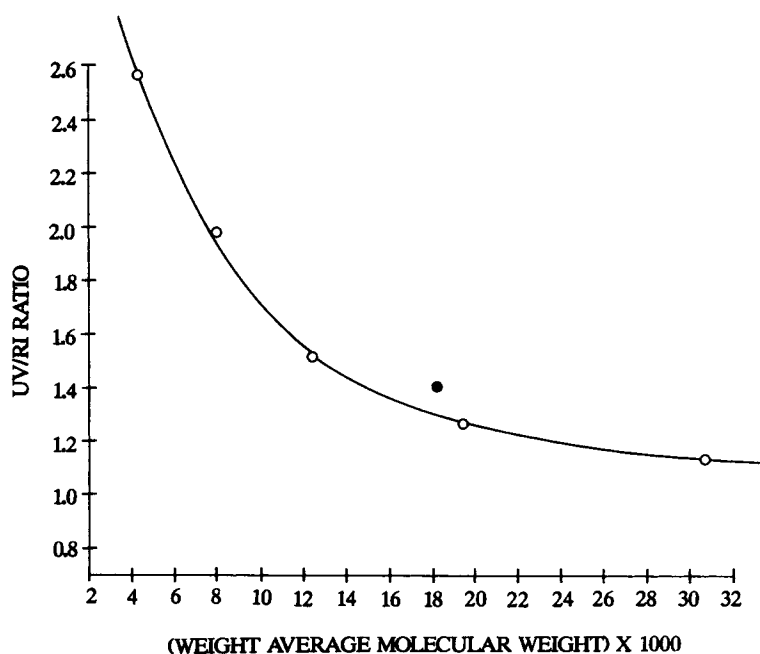


Fig. 7(a). UV/RI ratio of peak maximum plotted vs. weight average molecular weight of oligomer 3 fractions: (●) parent polymer.

formation of Diels–Alder adducts from styrene monomer. These adducts are capable of initiating chain propagation and may ultimately appear as end-groups in the polymer.<sup>9,10</sup> Thus, oligomers of lower MW with a higher percentage of mass occupied by end groups exhibit the highest proportion of styrenic endgroups. The UV absorbing peaks observed in the low MW fraction are believed to be dimeric products formed by side reactions during Diels–Alder adduct formation.<sup>9</sup> Variations in the level of styrene would be expected to cause rather pronounced changes in the ultimate end-use properties of these oligomers. Since SCF fractionation allows for the selective removal of polymers from multicomponent mixtures, materials with much more precisely defined and controlled physical/chemical properties can be prepared.

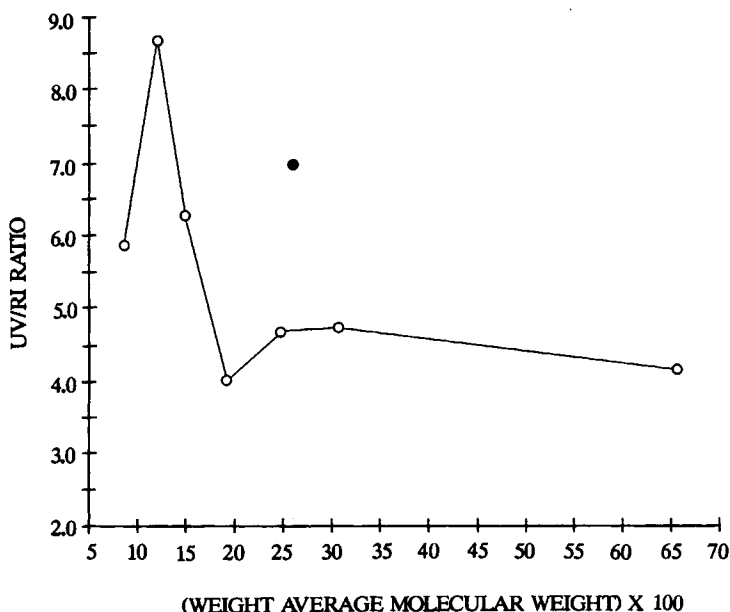


Fig. 7(b). UV/RI ratio of peak maximum plotted vs. weight average molecular weight of oligomer 2 fractions: (●) parent polymer.

## CONCLUSION

Supercritical fluid processing has been shown to be an effective method for purification and fractionation of synthetic polymers. By purifying and fractionating multicomponent polymer mixtures, it is possible to analyze in greater detail the physical and compositional changes which occur as a function of molecular weight. This in turn may allow for a more thorough understanding of the phenomena occurring during the polymerization process. It is believed that in future years, a greater demand for high performance materials will result in increased use of supercritical fluids for processing of synthetic polymers.

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