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### Ultrasonic Modification of Polymers. II. Degradation of Polystyrene, Substituted Polystyrene, and Poly(n-vinyl Carbazole) in the Presence of Flexible Chain Polymers

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## **Ultrasonic Modification of Polymers. II. Degradation of Polystyrene, Substituted Polystyrene, and Poly(n-vinyl Carbazole) in the Presence of Flexible Chain Polymers**

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### **A B S T R A C T**

Ultrasonic (20 kHz, 70 W) solution degradations of polystyrene, substituted polystyrenes, and poly(n-vinyl carbazole) have been carried in toluene and tetrahydrofuran at 27 and -20°C in the presence of flexible chain polymers. Polystyrene formed block copolymers at 27°C with stiff-chain polymer PVCz; however, in the presence of flexible chain polymers, e.g., poly(vinyl methyl ketone) or poly(vinyl methyl ether), there were no block copolymers formed. Poly(n-vinyl carbazole) does not seem to form any block copolymers at 27°C with flexible chain polymers, e.g., poly(octadecyl methacrylate) and poly(ethyl methacrylate). Poly(p-chlorostyrene) and poly(p-methoxystyrene) also do not form block copolymers at 27°C with poly(octadecyl methacrylate) but do so with poly(hexadecyl methacrylate). It is quite possible that these may only be blends of two homopolymers. Poly(octadecyl methacrylate) does yield a block copolymer when sonicated at -15°C with poly(p-isopropyl  $\alpha$ -methylstyrene).

## INTRODUCTION

In an earlier report on the ultrasonic solution degradation of polystyrene in the presence of various poly(alkyl methacrylates) (PRMA) [1], it was shown that when the substituents R in PRMA were methyl, ethyl, isopropyl, n-butyl, isobutyl, or phenyl, scrambled copolymers with segments from PS and PRMA were obtained. However, when the substituents R in PRMA were cyclohexyl, benzyl, hexyl, isodecyl, lauryl, hexadecyl, octadecyl, or isobornyl, there were no sequence copolymers formed. The decrease in the intrinsic viscosity and shifts of their GPC chromatograms toward the low molecular weight end suggest that on sonification, PRMA samples with bulkier substituents do degrade and yield radicals which, however, do not recombine with those from polystyrene. Furthermore, degradation of polystyrene was found to be dependent on the chain stiffness of the poly(alkyl methacrylates).

With a view to extend these studies, ultrasonic solution degradation of polystyrene, substituted polystyrenes, and poly(n-vinyl carbazole) were carried out in the presence of flexible chain polymers. Results of these studies are reported here.

## EXPERIMENTAL

### Materials

Samples of polystyrene (Pressure Chemical Co.); poly(p-chloro-styrene), poly(p-methoxystyrene), poly(n-vinyl carbazole), poly(octadecyl methacrylate), poly(hexadecyl methacrylate) (Aldrich Chemical Co.); poly(p-isopropyl  $\alpha$ -methylstyrene) [2]; poly(vinyl methyl ketone) and poly(vinyl methyl ether) (Scientific Polymer) were used in the present studies.

### Degradation Procedure

Ultrasonic degradations of polymer solutions were carried out in a batch reactor (10 cm long, 5 cm diameter, 200 mL capacity), equipped with water jackets to maintain a 2°C temperature within, and measured with a Ni-Cr alloy probe and a Comark digital thermometer [1]. Prior to subjecting the polymer solutions to ultrasonic treatments, these were purged with nitrogen for a period of 30 min. The sealed aluminum reactor was screwed onto a threaded nodal point on a 1.25 cm diameter disruptor horn (Heat Systems, Model 375A with nominal frequency of 20 kHz) where attachment produces no damping. An ultrasonic intensity of 70 W was adjusted by using the calibration curve of meter reading, the power control setting, and the power output in watts provided by the manufacturer. After sonicating the polymer solution for a desired period of time, it was transferred to a 1-L beaker and the solvent was removed by evaporation. The dried

products were subjected to fractionation for the removal of homopolymers using different solvent/nonsolvent systems. Solvent pairs were chosen in such a way that each solvent dissolved only one of the polymer and acted as a nonsolvent for the other. All products (homopolymers as well as block copolymers) recovered after fractionation were analyzed by infrared (IR) gel permeation chromatography (GPC) and viscometry.

### Characterization of Polymers

#### IR Analyses

The IR spectra of polymers were recorded from thin films (prepared on KBr disks) on a Beckman spectrophotometer Model 4250.

#### Viscosity Calculations

Calculations of the intrinsic viscosity of sonicated polymers and block copolymers were carried out in THF by making use of the flow time measurement data obtained with Ubbelohde viscometers at 25°C for at least three concentrations. Knowing the flow time of the solvent THF and the solutions, the computation of the intrinsic viscosity ( $\eta$ ) was carried out with

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (1)$$

where

$$\eta_{sp}/c = \left( \frac{\text{flow time of solution}}{\text{flow time of solvent}} - 1 \right)$$

Huggins coefficient  $k_H$  is related to  $[\eta]$  by

$$(\eta_{sp}/c) = [\eta] + k_H [\eta]^2 c \quad (2)$$

Viscosity measurements of the untreated homopolymers were also carried out in other solvents for which Mark-Houwink constants  $K$  and  $a$  are reported in the literature [3].

#### Gel Permeation Chromatographic Analyses

Molecular weight distributions of polymers were carried out with a Waters Associates GPC [equipped with a high pressure solvent delivery system (Model 6000 A), ultraviolet absorbance detector (Model 440), and a differential refractometer (model R401)] operated at 25°C. The separating system consisted of four  $\mu$ -Styragel columns

connected in series, each packed with cross-linked polystyrene gel (by the Waters method) having pore sizes of 500,  $1 \times 10^3$ ,  $1 \times 10^4$ , and  $1 \times 10^5$  Å, respectively. The flow of solvent, tetrahydrofuran, was maintained at 1 mL/min while the concentration of polymer solution was limited to 0.2% in order to render negligible, "concentration effects" on the peak position in the chromatograms. Calibration of the instrument was performed with standard polystyrene samples. The calibration curve relating elution volume  $V_e$  and molecular weight  $M$  yielded the relation

$$\ln M = 24.03 - 0.44V_e \quad (3)$$

Similarly, calibration curves relating  $V_e$  and  $M$  for poly(p-chloro-styrene) (Eq. 4); poly(p-methoxystyrene) (Eq. 5); poly(n-vinyl carbazole) (Eq. 6); poly(p-isopropyl  $\alpha$ -methylstyrene) (Eq. 7); poly(hexadecyl methacrylate), and poly(octadecyl methacrylate) (Eq. 8); and poly(vinyl methyl ketone) and poly(vinyl methyl ether) (Eq. 9) are as follows:

$$\ln M = 25.355 - 0.496V_e \quad (4)$$

$$\ln M = 24.93 - 0.456V_e \quad (5)$$

$$\ln M = 33.68 - 0.807V_e \quad (6)$$

$$\ln M = 24.03 - 0.44V_e \quad (7)$$

$$\ln M = 28.72 - 0.56V_e \quad (8)$$

$$\ln M = 27.54 - 0.56V_e \quad (9)$$

With the help of Eqs. (3) to (9), weight-average ( $\overline{M}_w$ ) and number-average ( $\overline{M}_n$ ) molecular weights of the homopolymers were computed from the uncorrected GPC chromatograms using the summation method [4]. The molecular weights of the copolymer were assumed to be the weighted averages of the log molecular weights of the homopolymers of the constituent comonomers. For example, in the case of a block copolymer of polystyrene and poly(methyl methacrylate),  $\overline{M}_w$  and  $\overline{M}_n$  values were computed using the polystyrene calibration curve ( $\overline{M}_w(\text{PS})$ ;  $\overline{M}_n(\text{PS})$ ) as well as with that of PMMA ( $\overline{M}_w(\text{PMMA})$ ;  $\overline{M}_n(\text{PMMA})$ ).

Knowing the composition of the block copolymer, molecular weights were then computed as follows:

$$\log \bar{M}_w = X_{PS} \log \bar{M}_{w(PS)} + X_{PMMA} \log \bar{M}_{w(PMMA)} \quad (10)$$

$$\log \bar{M}_n = X_{PS} \log \bar{M}_{n(PS)} + X_{PMMA} \log \bar{M}_{n(PMMA)} \quad (11)^*$$

where  $\bar{M}_w$  and  $\bar{M}_n$  are molecular weights of the block copolymer, and  $X_{PS}$  and  $X_{PMMA}$  are weight fractions of PS and PMMA, respectively, in the block copolymer ( $X_{PS} + X_{PMMA} = 1$ ). A similar approach has been suggested by Runyon et al. [5]. Copolymer molecular weights have not been computed from combined GPC-intrinsic viscosity data using the universal calibration curve as suggested by Ho-Duc and Prud'homme [6] because the work of Dondos et al. [7] and Tung [8] has shown that for block copolymers (in good solvents), the weighted average method is acceptable.

## RESULTS AND DISCUSSION

### Polystyrene (PS) and Poly(vinyl carbazole)(PVCz)

2.1 g PS ( $\bar{M}_w = 1.8 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 1.28$ ,  $[\eta] = 4.8$  dL/g) and 2.0 g PVCz ( $\bar{M}_w = 1.5 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 19.7$ ,  $[\eta] = 1.45$  dL/g,  $k_H = 0.43$ ) were dissolved in a 175 mL mixture (75% toluene + 25% THF) and purged with nitrogen for 30 min prior to ultrasonic treatment at 27°C for a period of 60 min. The resulting product was dried by evaporating the solvent at room temperature. Extraction with cyclohexane (800 mL), which is a solvent for PS but a nonsolvent for PVCz, yielded 100 mg of PS ( $\bar{M}_w = 2.65 \times 10^5$ ,  $\bar{M}_n = 1.1 \times 10^5$ ) while on subsequent washings with 800 mL toluene, 2.6 g of PS-PVCz copolymer ( $\bar{M}_w = 7.2 \times 10^5$ ,  $\bar{M}_n = 3.06 \times 10^5$ ,  $[\eta] = 3.2$  dL/g,  $k_H = 0.51$ ) was recovered, leaving behind 1.4 g of PVCz ( $\bar{M}_w = 1.55 \times 10^5$ ,  $\bar{M}_n = 8.35 \times 10^4$ ). GPC chromatograms of untreated homopolymers, unspent homopolymers recovered after ultrasonic treatment, and the block copolymer PS-PVCz are shown in Fig. 1. The IR spectrum of the toluene-soluble PS-PVCz copolymer (Fig. 2) showed the presence of both components; viz. PS and PVCz. From knowledge of the weights of the starting and end products, the composition of the block copolymer

\*Equation (11) in Part I of this series (S. L. Malhotra and J. M. Gauthier, *J. Macromol. Sci.-Chem.*, **A18**(5), 783-816, 1982) should be the same as Eq. (11) as presented above.

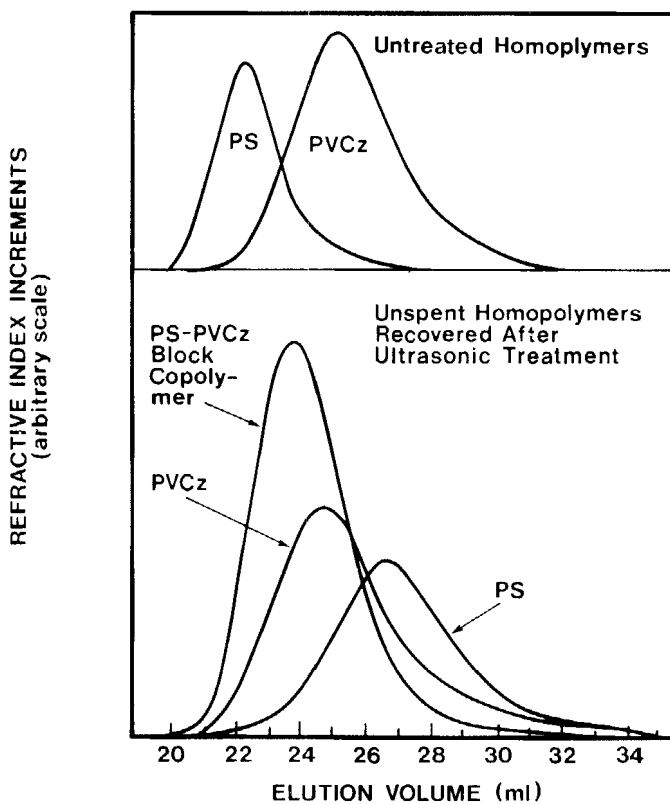


FIG. 1. GPC chromatograms of polymers in the ultrasonic solution (2.35%) degradation of PS and PVCz at 27°C for a period of 60 min.

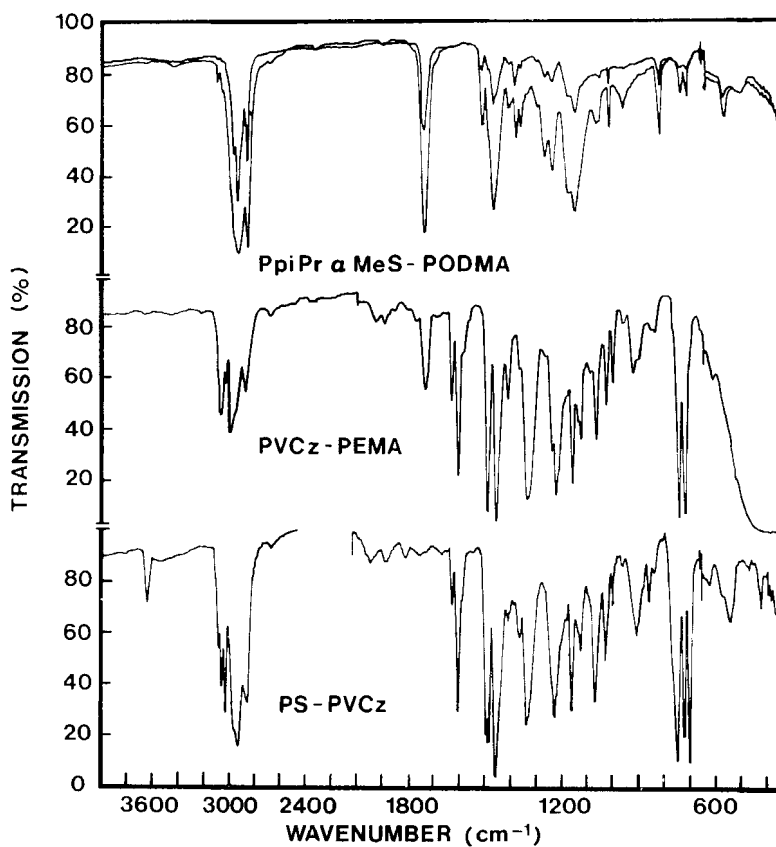


FIG. 2. IR spectra of block copolymers; viz. PS-PVCz, PVCz-PEMA, and PpiPr $\alpha$ MeS-PODMA.



TABLE 1. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PS

No.	Irradiation time (min)	Temperature (°C)	$\bar{M}_w \times 10^{-1}$ (GPC)	$\bar{M}_n \times 10^{-4}$ (GPC)	$\bar{M}_w/\bar{M}_n^a$	S min <sup>-1</sup>
-	-	-	180	140	1.28	-
X-253	30	27	88.2	60.5	1.45	0.044
X-248	60	27	60.5	42.5	1.4	0.038
X-242	120	27	52.5	35.0	1.5	0.025
X-249	180	27	48.6	32.5	1.5	0.018
X-250	240	27	44.1	29.5	1.5	0.015
X-251	390	27	31.5	21.0	1.5	0.014
X-252	480	27	25.0	18.0	1.4	0.014
X-262	15	-20	68.0	44.0	1.55	0.145
X-257	30	-20	53.5	40.0	1.34	0.083
X-258	60	-20	41.0	25.0	1.64	0.077
X-259	120	-20	30.0	17.8	1.5	0.056
X-260	180	-20	19.0	12.5	1.5	0.055
X-261	240	-20	15.0	10.0	1.5	0.053

<sup>a</sup> $\bar{M}_w/\bar{M}_n$  value of 1.28 for PS standard  $\bar{M}_w = 1.8 \times 10^6$  is lower than those published earlier.

TABLE 2. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PVCz

No.	Irradiation time (min)	Temperature (°C)	$\bar{M}_w \times 10^{-4}$ (GPC)	$\bar{M}_n \times 10^{-4}$ (GPC)	$\bar{M}_w/\bar{M}_n$	S min <sup>-1</sup>
-	-	-	150	7.65	19.7	-
X-98	60	27	59.5	3.95	15.1	0.016
X-99	120	27	52.5	4.65	11.4	0.005
X-100	180	27	39.0	3.5	11.1	0.006
X-101	240	27	30.0	3.1	9.65	0.006
X-102	360	27	16.5	2.5	6.63	0.006
X-103	480	27	12.0	2.7	4.5	0.004
X-264	30	-20	50.0	6.8	7.4	0.004
X-265	60	-20	20.5	2.9	7.15	0.027
X-266	120	-20	16.5	3.35	4.85	0.011
X-267	180	-20	10.0	1.8	5.57	0.018
X-268	240	-20	6.5	1.3	5.0	0.020

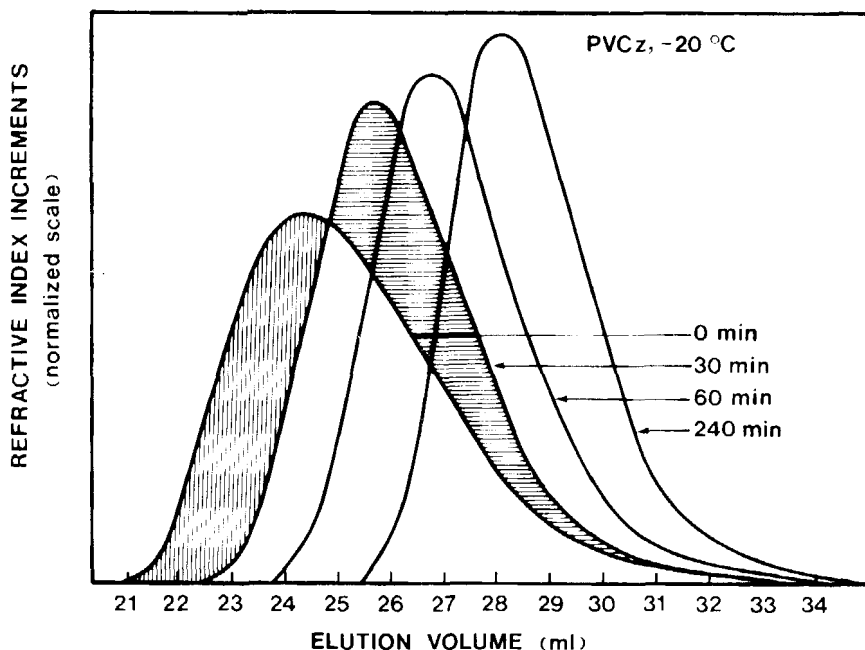


FIG. 3. Normalized GPC chromatograms of undegraded (0 min) and degraded PVCz samples on ultrasonic treatments at  $-20^{\circ}\text{C}$  for various periods of time.

was calculated to be 80% PS and 20% PVCz. This suggests that during the solution degradation of PS in the presence of PVCz, the average number of chain scissions  $S$  (where  $S = [(\bar{M}_n)_0 / (\bar{M}_n)_t] - 1$ ) is higher for the former polymer. In order to verify this hypothesis, ultrasonic solution degradations of PS and PVCz were carried out in THF at 27 and  $-20^{\circ}\text{C}$ . The degraded polymers were analyzed by GPC to gather overall  $(\bar{M}_n)_0$  and  $(\bar{M}_n)_t$  values presented in Table 1 (PS) and Table 2 (PVCz). These data clearly show that under identical conditions  $S \text{ min}^{-1}$  values for PS are always higher than those for PVCz. These calculations of  $S \text{ min}^{-1}$  are based on the conventional method of using overall values of  $(\bar{M}_n)_0$ ,  $(\bar{M}_n)_t$ ; however, as in ultrasonic solution degradations, only a part of the polymer is involved, initially, use of overall molecular weights in the calculation of  $S \text{ min}^{-1}$  is questionable. In order to circumvent this objection, an alternate approach of analyses [9] was used where the normalized GPC chromatograms (surface area under each chromatogram being the same) of degraded polymers were compared with that of the original polymer as shown in Fig. 3 for

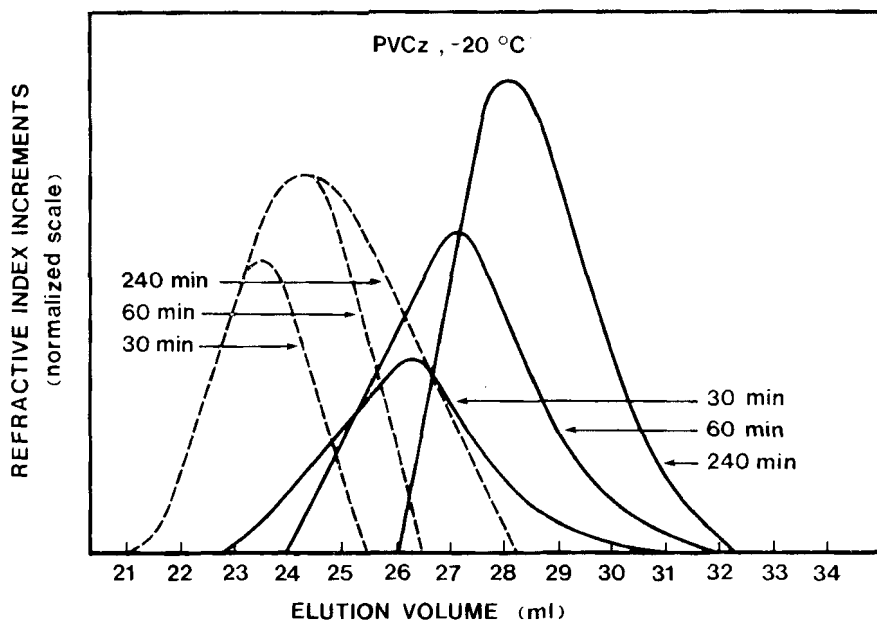


FIG. 4. Graphical method of analysis by which GPC distribution curves are broken down into their components. Case of PVCz subjected to ultrasonic treatments at  $-20^{\circ}\text{C}$  for various periods of time.

the case of PVCz at  $-20^{\circ}\text{C}$ . One notes that in the first 30 min of ultrasonic degradation, the area marked with vertical hash lines has disappeared from the original distribution and has reappeared elsewhere, possibly that marked with horizontal hash lines. On converting these areas into distributions (Fig. 4), one can readily visualize the changes resulting from the decomposition of higher molecular weight species. The areas under the decomposed components of the polymer for 30, 60, and 240 min in the case of PVCz (Fig. 4) correspond to 36, 63, and 82.5% of the original polymer, respectively. Making use of the  $(\bar{M}_n)_0$  and  $(\bar{M}_n)_t$  values in conjunction with the weight fraction

( $\alpha$ ) of that part of the polymer which is involved in degradation, normalized values of  $S'$  are calculated as follows:  $S' = (\alpha)[(\bar{M}_n)_0/(\bar{M}_n)_t] - 1$ .

These are presented in Table 3 (PS,  $27^{\circ}\text{C}$ ), Table 4 (PS,  $-20^{\circ}\text{C}$ ), Table 5 (PVCz,  $27^{\circ}\text{C}$ ), and Table 6 (PVCz,  $-20^{\circ}\text{C}$ ). These results show that at  $27^{\circ}\text{C}$  as well as at  $-20^{\circ}\text{C}$  there are more scissions per chain in PVCz compared to that for PS.  $S \text{ min}^{-1}$  and  $S' \text{ min}^{-1}$  values for PS computed using two different approaches do not differ by much. However,  $S' \text{ min}^{-1}$  for PVCz increases significantly when computed using only that part of the polymer which has participated in degradation.

TABLE 3. Ultrasonic Solution (2% THF) Degradation of PS at 27°C

No.	Irradiation time (min)	Weight fraction ( $\alpha$ )	Before degradation			After degradation			S' normalized values	S' min <sup>-1</sup>
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$		
X-253	30	0.40	194	185	1.05	74	54.2	1.36	0.97	0.032
X-248	60	0.70	175	163	1.07	61.5	45.4	1.35	1.80	0.030
X-242	120	0.94	158	141	1.12	54.1	35.0	1.55	2.85	0.024
X-249	180	1.0	157	138	1.14	48.6	32.5	1.5	3.25	0.018
X-250	240	1.0	157	138	1.14	44.1	29.5	1.5	3.68	0.015
X-251	390	1.0	157	138	1.14	31.5	21.0	1.5	5.57	0.014
X-252	480	1.0	157	138	1.14	25.0	18.0	1.4	6.66	0.014

TABLE 4. Ultrasonic Solution (2% THF) Degradation of PS at -20°C

No.	Irradiation time (min)	Weight fraction ( $\alpha$ )	Before degradation			After degradation			S' normalized values	S' $\text{min}^{-1}$
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$		
X-262	15	0.68	180	168	1.07	73.4	47.1	1.56	1.74	0.116
X-257	30	0.88	164	147	1.12	67.0	40.0	1.68	2.36	0.079
X-258	60	0.98	157	138	1.14	43.0	25.7	1.67	4.26	0.071
X-259	120	1.0	157	138	1.14	30.0	17.8	1.68	6.75	0.056
X-260	180	1.0	157	138	1.14	19.0	12.5	1.5	10.00	0.055
X-261	240	1.0	157	138	1.14	15.0	10.0	1.5	12.80	0.053

TABLE 5. Ultrasonic Solution (2% THF) Degradation of PVCz at 27° C

No.	Irradiation time (min)	Weight fraction ( $\alpha$ )	Before degradation			After degradation			S' normalized values	S' min <sup>-1</sup>
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$		
X-98	60	0.30	355	225	1.58	63	15.8	4.0	4.04	0.067
X-99	120	0.36	328	205	1.59	56.2	13.9	4.0	4.97	0.041
X-100	180	0.42	294	173	1.70	35.1	10.0	3.5	6.91	0.038
X-101	240	0.57	234	100	2.34	28.8	0.86	3.33	6.01	0.025
X-102	360	0.58	240	125	1.92	20.0	0.75	2.67	9.04	0.025
X-103	480	0.725	200	81.4	2.46	13.7	0.47	2.9	11.67	0.024

TABLE 6. Ultrasonic Solution (2% THF) Degradation of PVCz at -20°C

No.	Irradiation time (min)	Weight fraction ( $\alpha$ )	Before degradation		After degradation		$S'$ normalized values	$S'$ $\text{min}^{-1}$		
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$				
X-264	30	0.36	324	200	1.62	50.3	14.3	3.52	4.68	0.156
X-265	60	0.63	226	111	2.0	21.6	5.9	3.66	11.30	0.188
X-266	120	0.64	221	100	2.2	12.9	5.35	2.40	11.50	0.096
X-267	180	0.69	209	77.5	2.7	6.67	2.59	2.57	20.65	0.114
X-268	240	0.825	178	50.8	3.5	6.32	2.58	2.45	14.86	0.062



It would appear that although PVCz degrades better than PS, their radical-radical recombination is not favorable. Thus a block copolymer of PS-PVCz with a higher content of PVCz is not possible with the ultrasonic technique.

In an earlier study [1] it was reported that in ultrasonic solution degradation of PS in the presence of poly(octadecyl methacrylate) (PODMA), there was no block copolymer formed in spite of the fact that the two homopolymers did degrade. It was postulated that radicals formed during the degradation process did not recombine. In order to verify the failure of radical-radical recombination in such reactions, block copolymerization of PODMA was attempted with PVCz.

### PODMA and PVCz

1.0 g PVCz ( $\bar{M}_w = 1.5 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 19.7$ ,  $[\eta] = 1.46$  dL/g,  $k_H = 0.43$ ) and 1.0 g PODMA ( $\bar{M}_w = 6.7 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 6.0$ ,  $[\eta] = 0.49$  dL/g,  $k_H = 0.43$ ) were dissolved in a 175-mL mixture (75% toluene + 25% THF) and purged with nitrogen for 30 min prior to ultrasonic treatment at 27°C for a period of 60 min. The resulting product was dried by evaporating the solvent at room temperature. Extraction with 700 mL n-butylacetate yielded 1.0 g of PODMA with a lower molecular weight than that of the starting material. Subsequent extractions with N,N-dimethylformamide yielded 350 mg of PVCz ( $\bar{M}_w = 1.04 \times 10^6$ ,  $\bar{M}_n = 1.29 \times 10^5$ ), leaving behind 650 mg PVCz ( $\bar{M}_w = 1.95 \times 10^6$ ,  $\bar{M}_n = 3.24 \times 10^5$ ,  $[\eta] = 1.10$ ,  $k_H = 0.52$ ).  $\bar{M}_w$  and  $\bar{M}_n$  values were computed from the GPC chromatograms shown in Fig. 5.

The absence of block copolymer in this experiment is attributed to the lack of degradation of the two homopolymers, which therefore do not generate enough radicals for recombination. As PVCz degrades well in the presence of PS but not in the presence of PODMA which carries a long-chain substituent, it was thought of interest to replace PODMA with poly(ethyl methacrylate) (PEMA).

### PVCz and PEMA

In the first experiment, 1.0 g PVCz ( $\bar{M}_w = 1.5 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 19.7$ ) and 2.0 g PEMA ( $\bar{M}_w = 3.46 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 3.0$ ) were dissolved in 175 mL THF, purged with dry nitrogen for 30 min, and sonicated at 27°C for a period of 420 min. Evaporation of the solvent yielded dry products. Extraction with a 1000-mL mixture of isopropanol

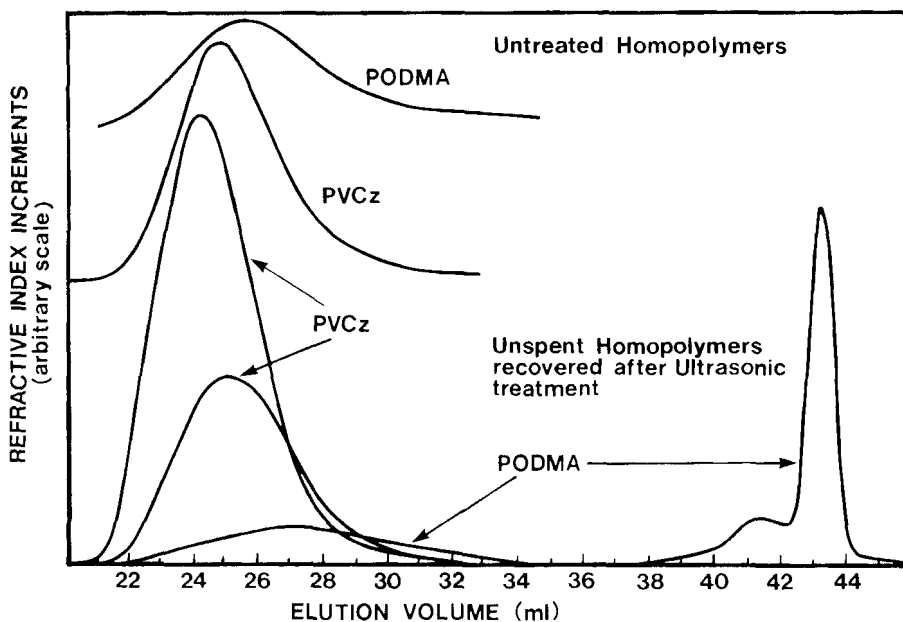


FIG. 5. GPC chromatograms of polymers in the ultrasonic solution (1.14%) degradation of PVCz and PODMA at 27°C for a period of 60 min.

(800 mL) and methyl ethyl ketone (200 mL) yielded 1.8 g PEMA ( $\bar{M}_w = 1.62 \times 10^5$ ,  $\bar{M}_n = 7.64 \times 10^4$ ), while subsequent washings with 700 mL N,N-dimethylformamide recovered the remaining 1.2 g polymer mixture ( $\bar{M}_w = 3.43 \times 10^5$ ,  $\bar{M}_n = 6.95 \times 10^4$ ), leaving nothing behind. It is quite possible that the polymer mixture soluble in N,N-dimethylformamide is a mixture of PVCz and PVCz-PEMA block copolymer. The IR spectrum of this mixture (Fig. 2) showed the presence of both components.  $\bar{M}_w$  and  $\bar{M}_n$  values of the homopolymers were computed from the GPC chromatograms shown in Fig. 6.

In the second experiment, 1.4 g PVCz and 1.3 g PEMA ( $[\eta] = 0.77$  dL/g,  $k_H = 0.3$ ) were dissolved in 175 mL THF and sonicated at 27°C for 420 min. Using similar extraction procedures, 1.15 g PEMA ( $\bar{M}_w = 1.46 \times 10^5$ ,  $\bar{M}_n = 6.4 \times 10^4$ ,  $[\eta] = 0.38$  dL/g, and  $k_H = 0.47$ ) and a 1.55-g mixture of PVCz and PVCz-PEMA block ( $\bar{M}_w = 2.37 \times 10^5$ ,  $\bar{M}_n = 5.06 \times 10^4$ ,  $[\eta] = 0.46$  dL/g, and  $k_H = 0.52$ ) were recovered.

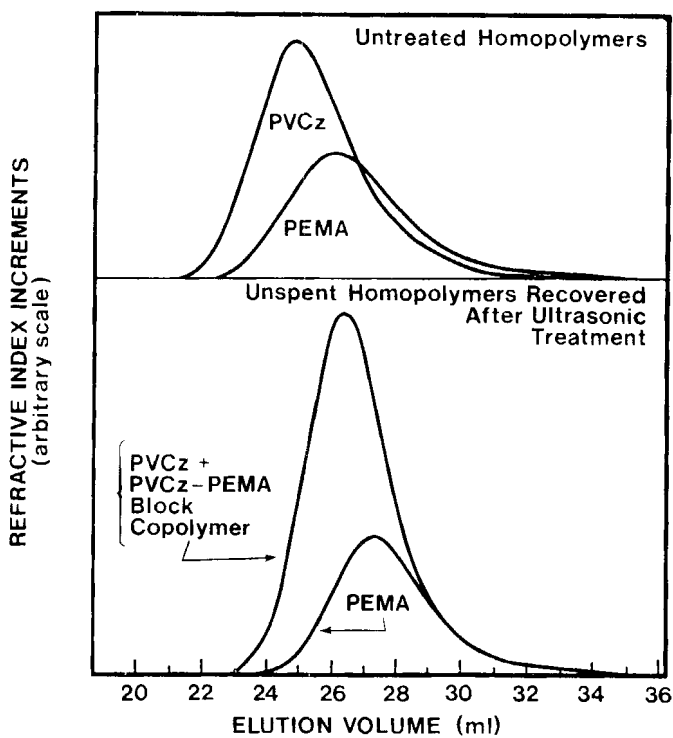


FIG. 6. GPC chromatograms of polymers in the ultrasonic solution (1.71%) degradation of PVCz and PEMA at 27°C for a period of 420 min. PVCz/PEMA = 0.5.

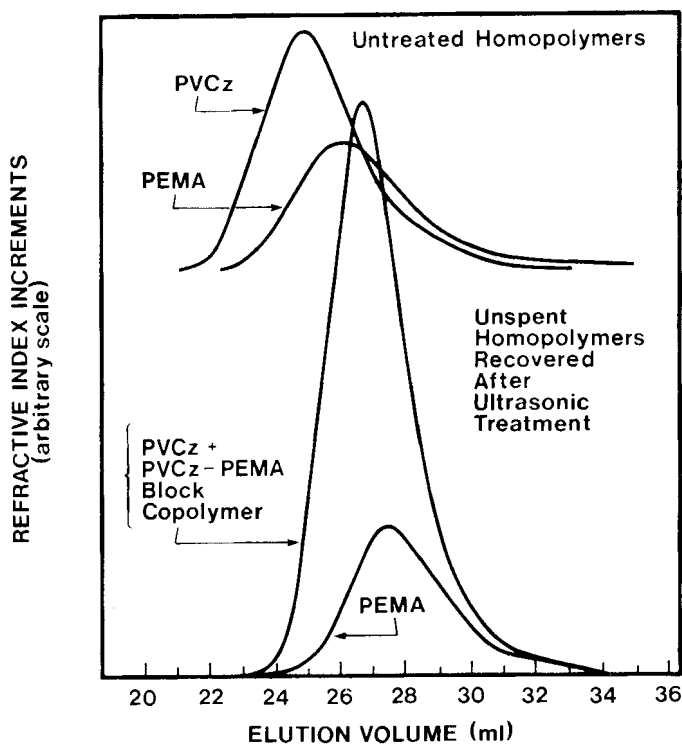


FIG. 7. GPC chromatograms of polymers in the ultrasonic solution (1.54%) degradation of PVCz and PEMA at 27°C for a period of 420 min. PVCz/PEMA = 1.08.

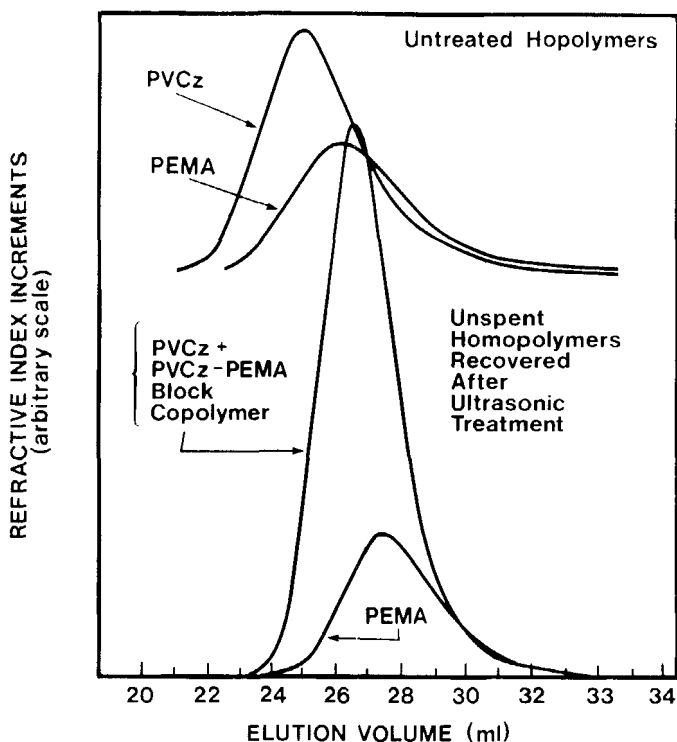


FIG. 8. GPC chromatograms of polymers in the ultrasonic solution (1.48%) degradation of PVCz and PEMA at 27°C for a period of 420 min. PVCz/PEMA = 0.53.

$\bar{M}_w$  and  $\bar{M}_n$  values listed here were computed from the GPC chromatogram shown in Fig. 7.

In the third experiment, 900 mg PVCz and 1.7 g PEMA were dissolved in 175 mL THF and sonicated at 27°C for a period of 420 min. Using the isopropanol and methyl ethyl ketone mixture, 1.6 g PEMA ( $\bar{M}_w = 1.5 \times 10^5$ ,  $\bar{M}_n = 7.13 \times 10^4$ ) and a 1.0-g blend of PVCz and PVCz-PEMA block ( $\bar{M}_w = 2.7 \times 10^5$ ,  $\bar{M}_n = 6.39 \times 10^4$ ) were obtained.

$\bar{M}_w$  and  $\bar{M}_n$  values were computed from the GPC chromatograms shown in Fig. 8.

These experiments show that degradations of PVCz and PEMA do take place but radical-radical recombination is not favored. Similar results were obtained when ultrasonic block copolymerization of PS was attempted with poly(vinyl methyl ketone) (PVMK) and poly(vinyl methyl ether) (PVME).

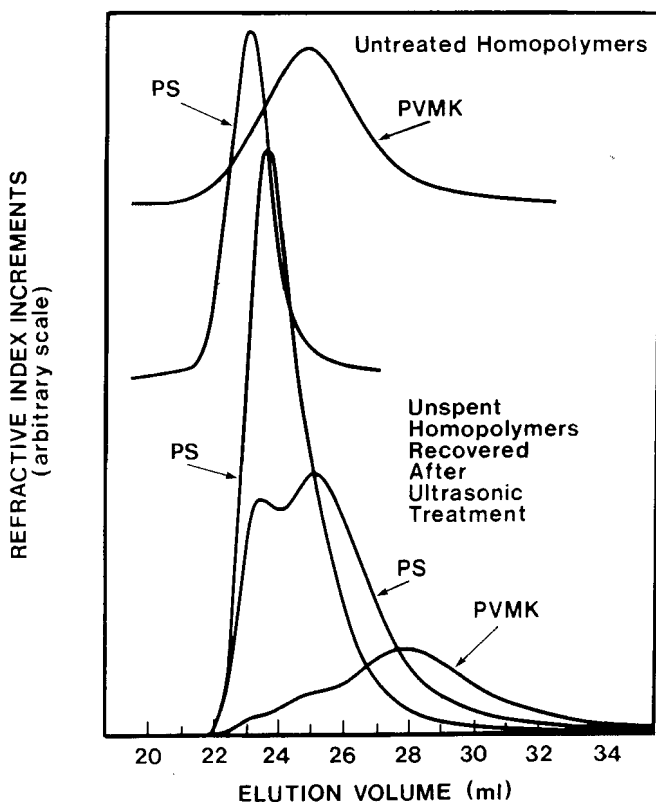


FIG. 9. GPC chromatograms of polymers in the ultrasonic solution (2.51%) degradation of PS and PVMK at 27°C for a period of 210 min.

### PS and PVMK

2.0 g PS ( $\bar{M}_w = 9.0 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1.3$ ) and 2.4 g PVMK ( $\bar{M}_w = 1.07 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 2.15$ ) were dissolved in 175 mL THF, purged with nitrogen for 30 min, and sonicated at 27°C for a period of 210 min. Evaporation of solvent yielded the dried product which, when subjected to extraction with 700 mL cyclohexane, gave 500 mg PS ( $\bar{M}_w = 5.02 \times 10^5$ ,  $\bar{M}_n = 2.46 \times 10^5$ ) while subsequent washings with 700 mL acetone recovered 2.4 g PVMK ( $\bar{M}_w = 3.38 \times 10^5$ ,  $\bar{M}_n = 6.3 \times 10^4$ ), leaving behind 1.5 g PS ( $\bar{M}_w = 6.83 \times 10^5$ ,  $\bar{M}_n = 4.9 \times 10^5$ ,  $[\eta]$

= 2.0 dL/g, and  $k_H = 0.37$ ). This indicates that PS does not degrade well in the presence of PVMK and no radical-radical recombination occurs.  $\bar{M}_w$  and  $\bar{M}_n$  were computed from the GPC chromatograms shown in Fig. 9.

### PS and PVME

2.0 g PS ( $\bar{M}_w = 9.0 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1.3$ ) and 5.0 g PVME ( $\bar{M}_w = 1.17 \times 10^5$ ,  $\bar{M}_n = 3.0 \times 10^4$ ) were dissolved in 175 mL toluene, purged with nitrogen, and sonicated at 27°C for a period of 210 min. Evaporation of the solvent yielded dried products which when subjected to extraction with 700 mL cyclohexane gave negligible amounts of PS while subsequent washings with a 50:50 mixture of acetone and cyclohexanol recovered 5.0 g of PVME with  $\bar{M}_w$  and  $\bar{M}_n$  values similar to those of untreated PVME, leaving behind 2.05 g PS ( $\bar{M}_w = 4.12 \times 10^5$ ,  $\bar{M}_n = 2.4 \times 10^5$ ,  $[\eta] = 1.5$  dL/g, and  $k_H = 0.53$ ). These molecular weights were computed from the GPC chromatograms shown in Fig. 10.

### Poly(p-chlorostyrene) (PpClS) and PODMA

2.0 g PpClS ( $\bar{M}_w = 1.8 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 1.4$ ,  $[\eta] = 2.42$  dL/g,  $k_H = 0.34$ ) and 2.5 g PODMA ( $\bar{M}_w = 6.7 \times 10^5$ ,  $[\eta] = 0.49$  dL/g) were dissolved in 175 mL toluene, purged with nitrogen, and sonicated at 27°C for a period of 180 min. Evaporation of the solvent yielded dried products which when subjected to fractionation with 700 mL methyl ethyl ketone gave 2.0 g PpClS with similar molecular weights ( $[\eta] = 2.15$  dL/g and  $k_H = 0.40$ ) as those of the untreated PpClS while subsequent washings with a 50:50 mixture of heptane and acetone recovered the homopolymer PODMA ( $\bar{M}_w = 2.6 \times 10^5$ ,  $\bar{M}_n = 9.8 \times 10^4$ ,  $[\eta] = 0.28$  dL/g). These molecular weights were computed from the GPC chromatograms shown in Fig. 11.

### Poly(p-chlorostyrene) (PpClS) and Poly(hexadecyl methacrylate) (PHDMA)

2.0 g PpClS ( $\bar{M}_w = 1.8 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 1.4$ ,  $[\eta] = 2.42$  dL/g, and  $k_H = 0.34$ ) and 4.0 g PHDMA ( $\bar{M}_w = 1.53 \times 10^6$ ,  $\bar{M}_w/\bar{M}_n = 5.8$ ,  $[\eta] = 0.51$  dL/g,  $k_H = 0.48$ ) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for a period of 210 min.

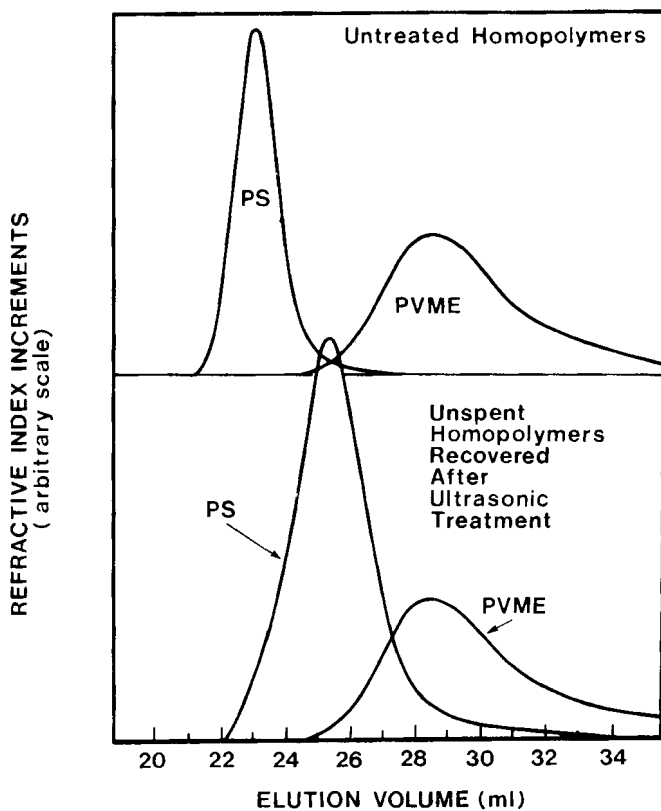


FIG. 10. GPC chromatograms of polymers in the ultrasonic solution degradation (4.0%) of PS and PVME at 27°C for a period of 210 min.



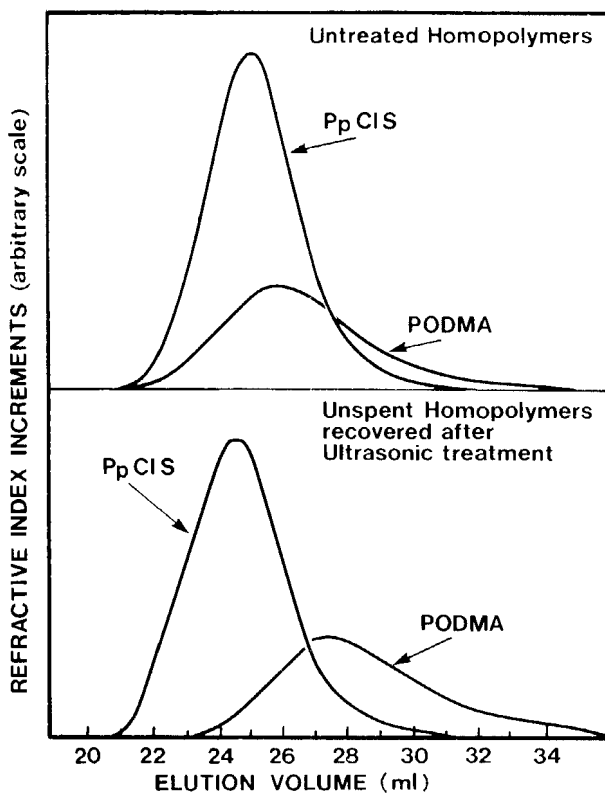


FIG. 11. GPC chromatograms of polymers in the ultrasonic solution (2.57%) degradation of PpClS and PODMA at 27°C for a period of 180 min.

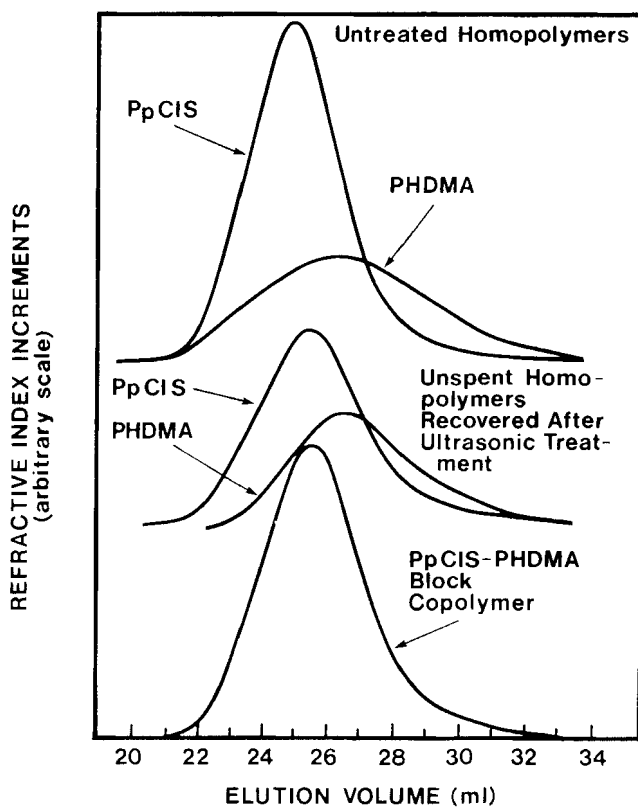


FIG. 12. GPC chromatograms of polymers in the ultrasonic solution (3.43%) degradation of PpCIS and PHDMA at 27°C for a period of 210 min.

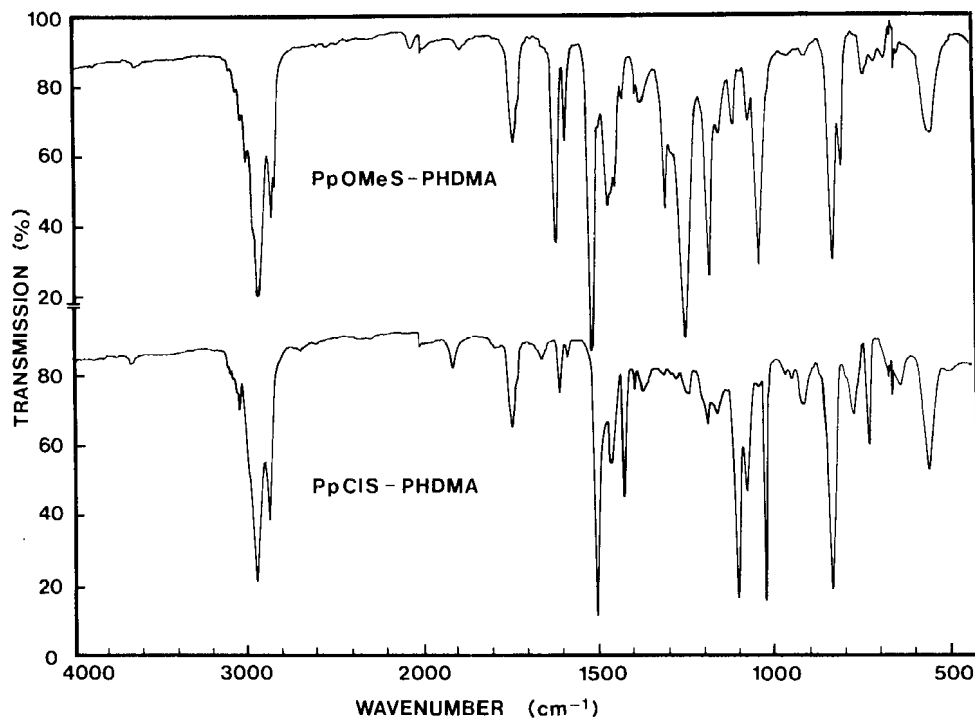


FIG. 13. IR spectra of PpClS-PHDMA and PpOMeS-PHDMA block copolymers.

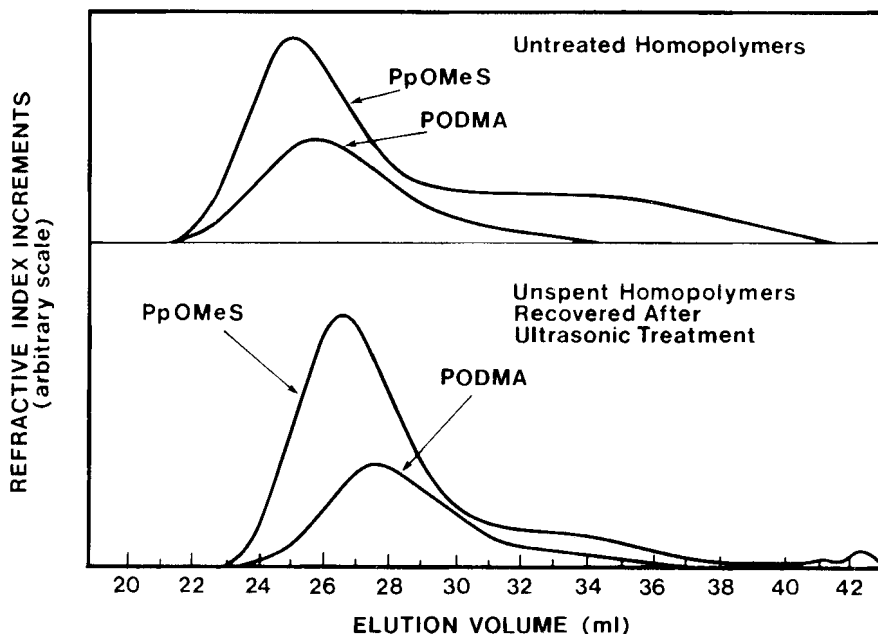


FIG. 14. GPC chromatograms of polymers in the ultrasonic solution (2.57%) degradation of PpOMeS and PODMA at 27°C for a period of 210 min.

Evaporation of the solvent yielded dried products which when subjected to fractionation with 700 mL methyl ethyl ketone gave 1.0 g PpClS ( $\bar{M}_w = 4.46 \times 10^5$ ,  $\bar{M}_n = 2.2 \times 10^5$ ,  $[\eta] = 1.3$  dL/g,  $k_H = 0.27$ ) while subsequent washings with heptane recovered 3.5 g PHDMA ( $\bar{M}_w = 1.32 \times 10^6$ ,  $\bar{M}_n = 4.42 \times 10^5$ ,  $[\eta] = 0.38$  dL/g,  $k_H = 0.7$ ). Molecular weights were computed from the GPC chromatograms shown in Fig. 12. The IR spectrum of the block copolymer (Fig. 13) showed the presence of both components which were found to be 67% PpClS and 33% PHDMA.

#### Poly(p-methoxystyrene) (PpOMeS) and PODMA

2.0 g PpOMeS ( $\bar{M}_w = 7.0 \times 10^5$ ,  $[\eta] = 0.86$  dL/g,  $k_H = 0.49$ ) and 2.5 g PODMA ( $\bar{M}_w = 6.7 \times 10^5$ ) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for a period of 180 min. Evaporation of THF yielded dried products which when subjected to fractionation with 700 mL methyl ethyl ketone yielded 2.0 g

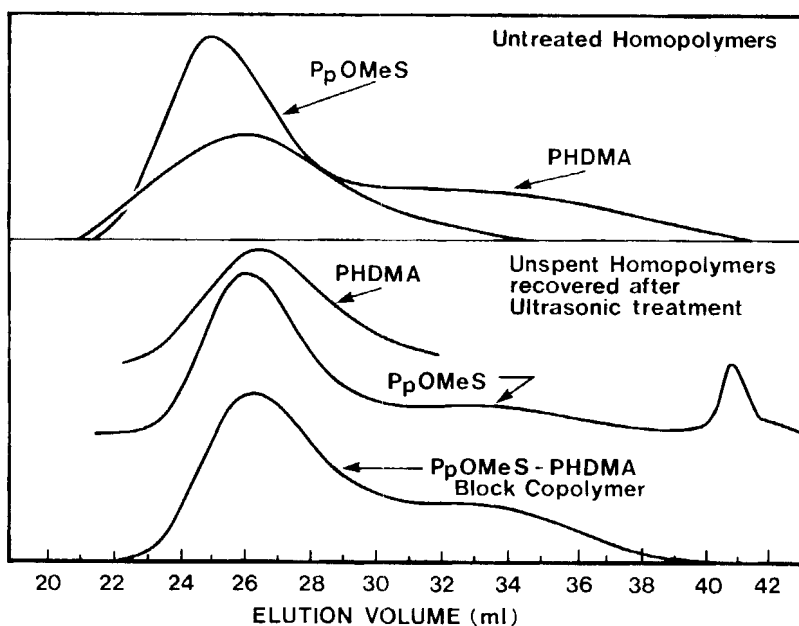


FIG. 15. GPC chromatograms of polymers in the ultrasonic solution (3.43%) degradation of PpOMeS and PHDMA at 27°C for a period of 210 min.

PpOMeS ( $\bar{M}_w = 3.37 \times 10^5$ ,  $[\eta] = 0.60$  dL/g,  $k_H = 0.34$ ) while subsequent washings with 50:50 mixture of heptane and acetone recovered 2.5 g PHDMA ( $\bar{M}_w = 6.13 \times 10^5$ ,  $\bar{M}_n = 8.08 \times 10^4$ ,  $[\eta] = 0.25$  dL/g).

Molecular weights were computed from the GPC chromatograms shown in Fig. 14.

#### PpOMeS and PHDMA

2.0 g PpOMeS ( $\bar{M}_w = 7.0 \times 10^5$ ,  $[\eta] = 0.86$  dL/g) and 4.0 g PHDMA ( $\bar{M}_w = 1.53 \times 10^6$ ,  $[\eta] = 0.51$  dL/g,  $k_H = 0.48$ ) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for a period of 210 min. Evaporation of solvent yielded dried product which when subjected to fractionation with 700 mL methyl ethyl ketone gave 1.625 g PpOMeS ( $\bar{M}_w = 3.23 \times 10^5$ ,  $[\eta] = 0.48$  dL/g,  $k_H = 0.30$ ).

These molecular weights were computed from the GPC chromatograms shown in Fig. 15. The IR spectrum of the PpOMeS-PHDMA block

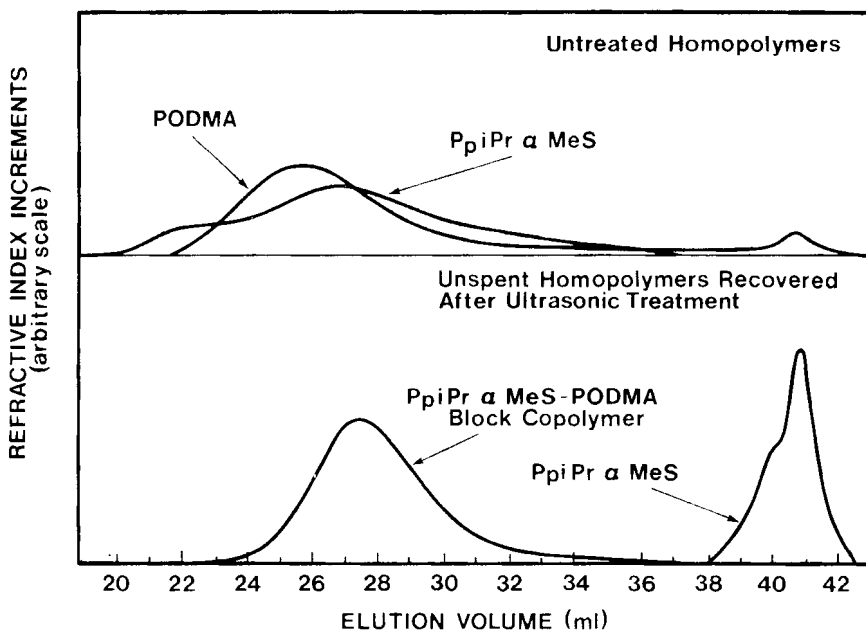


FIG. 16. GPC chromatograms of polymers in the ultrasonic solution (2.34%) degradation of PpiPr $\alpha$ MeS and PODMA at 27°C for a period of 275 min.

in Fig. 15 showed the presence of both components which were found to be 67% PpOMeS and 33% PHDMA from the material balance.

Poly(p-isopropyl  $\alpha$ -methylstyrene) (PpiPr $\alpha$ MeS) and PODMA

2.1 g PpiPr $\alpha$ MeS ( $\bar{M}_w = 1.0 \times 10^6$ ,  $[\eta] = 0.6$  dL/g) and 2.0 g PODMA ( $\bar{M}_w = 6.7 \times 10^5$ ,  $[\eta] = 0.49$  dL/g) were dissolved in 175 mL THF, purged with nitrogen for 30 min, and sonicated at -15°C for a period of 275 min. Evaporation of solvent yielded dried product which when subjected to fractionation with 700 mL cyclohexane gave 4.0 g of PpiPr $\alpha$ MeS-PODMA block copolymer ( $\bar{M}_w = 7.46 \times 10^5$ ,  $\bar{M}_n = 3.39 \times 10^5$ ,  $[\eta] = 0.36$ ) while subsequent washings with a 900-mL mixture of heptane (600 mL) and acetone (300 mL) recovered 100 mg PpiPr $\alpha$ MeS of very low molecular weight. These molecular weights were computed from the GPC chromatograms shown in Fig. 16.

The IR spectrum of PpiPr $\alpha$ MeS-PODMA (Fig. 2) showed the presence of both components which were 50% PpiPr $\alpha$ MeS and 50% PODMA from the material balance analysis. It would appear that at low temperatures the normally flexible chain PODMA becomes stiff enough to break and generate radicals which recombine with those from PpiPr $\alpha$ MeS to yield a block copolymer. It is also possible that at low temperature the improved efficiency of ultrasonic degradation (higher weight fraction of the polymers being involved in chain-breaking, thereby yielding more radicals) is responsible for the formation of block copolymers.

Mahabadi and O'Driscoll [10] have shown that in free radical polymerization of alkyl methacrylates (RMA), the termination rate constants depend on the size of the monomer. Relative values of  $k_{tRMA}/k_{tMMA}$  for the R substituents methyl, butyl, octyl, and dodecyl in the monomer RMA were reported to be  $100 \times 10^{-2}$ ,  $40.0 \times 10^{-2}$ ,  $12.88 \times 10^{-2}$ , and  $2.91 \times 10^{-2}$ , respectively. It was postulated that in RMA carrying bulkier substituents with a high hydrodynamic radius of chain-ends, diffusion-controlled termination is not favored. This may also explain the inability of PRMA to form block copolymers with PS, substituted PS, and PVCz when the substituents in the former were bulkier [1].

## CONCLUSIONS

1. Ultrasonic solution degradation of PS at 27°C in the presence of stiff chain polymers e.g., PVCz, results in the formation of a block copolymer. However, in the presence of flexible chain polymers, e.g., PVMK and PVME, there are no block copolymers produced. In the system PS and PVME, the absence of block copolymers may be explained as being due to the inability of PVME to degrade on account of its low molecular weight. In the other system (viz., PS and PVMK) where both polymers degrade, radical-recombination problems may be the reason for the absence of block copolymers.

2. Ultrasonic solution degradations of PVCz at 27°C in the presence of flexible chain polymers, e.g., PODMA and PEMA, also do not result in block copolymers, although with the latter polymer there might be some scrambling resulting in a block copolymer with very little PEMA content.

3. PpOMeS and PpClS solution degradations at 27°C in the presence of PODMA do not result in block copolymers. However, surprisingly, PHDMA does seem to produce block copolymers with PpClS and PpOMeS in spite of the fact that PODMA and PHDMA are both flexible chain polymers. It is quite possible that these may only be blends of two polymers rather than block copolymers.

4. The IR spectrum of the product obtained after ultrasonic solution degradation of PpiPr $\alpha$ MeS in the presence of PODMA at -15°C showed the presence of both components, indicating the possibility of

a block copolymer having been formed. It would appear that the normally flexible chain PODMA becomes stiff enough to break low temperatures and recombine with radicals from PpiPr<sub>2</sub>MeS to yield a block copolymer.

Studies are being pursued on the ultrasonic solution degradation of PODMA and other poly(alkyl methacrylates) at 27 and -20°C to determine their average number of chain scissions as a function of temperature. This is expected to provide answers regarding the ability of PODMA to form block copolymers at low temperatures and not at 27°C.

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#### REFERENCES

- [1] S. L. Malhotra and J. M. Gauthier, J. Macromol. Sci.-Chem., **A18**, 783 (1982).
- [2] J. Leonard and S. L. Malhotra, Ibid., **A11**, 2087 (1977).
- [3] J. Brandrup and E. H. Immergut (eds.), Polymer Handbook, 2nd ed., Wiley, New York, 1974.
- [4] Waters Associates, Gel Permeation Chromatograph Instruction Manual, Bull. No. 2, p. 2064, 1966.
- [5] J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, J. Appl. Polym. Sci., **13**, 2359 (1969).
- [6] N. Ho-Duc and J. Prud'homme, Macromolecules, **6**, 472 (1973).
- [7] A. Dondos, P. Rempp, and H. Benoit, Makromol. Chem., **130**, 233 (1969).
- [8] L. H. Tung, J. Appl. Polym. Sci., **24**, 953 (1979).
- [9] S. L. Malhotra, J. Hesse, and L. P. Blanchard, Polymer, **16**, 81 (1975).
- [10] H. K. Mahabadi and K. F. O'Driscoll, J. Polym. Sci., Polym. Lett. Ed., **14**, 671 (1976).

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