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## Radiation-Induced Cationic Oligomerization of $\alpha$ -Methylstyrene in Hydrocarbon Solutions

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### ABSTRACT

The radiation-induced cationic oligomerization of  $\alpha$ -methylstyrene was carried out in dilute hydrocarbon solutions at 0°C. Under rigorously dry conditions, oligomers are produced with relatively high yields in branched alkanes such as neopentane, 3-methylpentane, and dimethylbutanes. The oligomers contain alkyl groups derived from the solvent molecules. The average molecular weight of the oligomers decreases with decreasing monomer concentration. The formation of the oligomers is explained in terms of the chain transfer to the solvent molecules.

### INTRODUCTION

It has been established that the radiation-induced cationic polymerization of styrene derivatives proceeds by a cationic mechanism under rigorously dry conditions.<sup>(1)</sup> The initiating and propagating species responsible for the cationic polymerization

are in free-ion states and more reactive than those in ion-pair states, which are important when the polymerization is initiated by a catalyst. The polymerization is very sensitive to basic impurities, particularly to water. In the case of  $\alpha$ -methylstyrene ( $\alpha$ -MS), which is hardly polymerized by a radical mechanism, no detectable amount of polymer is produced unless the polymerization sample is rigorously dried.

In our earlier work on the radiation-induced cationic polymerization of  $\alpha$ -methylstyrene in saturated aliphatic hydrocarbon solutions it has been suggested that the chain transfer to the solvents occurs and results in a decrease in the average molecular weight of the products with decreasing monomer concentration.<sup>(2)</sup> Furthermore, the G value of the monomer consumption,  $G(-m)$ , increased with decreasing monomer concentration in branched alkanes such as neopentane, 3-methylpentane, and dimethylbutanes, whereas it decreased in hexane. It is expected, therefore, that low molecular weight oligomers may be produced with relatively high yields even in dilute solutions by using the branched alkanes as solvents. We have also reported that low molecular weight oligomers are produced when the rigorously dried monomer is irradiated in bulk at high temperature.<sup>(3)</sup>

In the present study the radiation-induced cationic oligomerization of  $\alpha$ -methylstyrene was examined in the dilute hydrocarbon solutions at 0°C and was compared with that in bulk at high temperature in order to obtain information about the chain transfer to the solvent molecules. It is interesting to note that the study on the radiation-induced cationic oligomerization

provides information about the reactivity of the propagating cations in free-ion states.

### EXPERIMENTAL

Purification and drying of  $\alpha$ -methylstyrene and the solvents, neopentane, 3-methylpentane, and 2,2- and 2,3-dimethylbutanes, were carried out as previously described.<sup>(2)</sup> The samples prepared as before were irradiated with  $^{60}\text{Co}$   $\gamma$  rays at a dose rate of  $5 \times 10^5$  rad/h for 1 h. The yield of oligomers was determined by weighing the irradiated sample before and after evaporating the solvent and remaining monomer under vacuum. The molecular weight distribution of the oligomers was measured by a gel permeation chromatograph (Toyo Soda HLC-801) in tetrahydrofuran with a differential refractometer and two 2-ft columns packed with TSK-Gel 1000H (nominal porosity, 40 A) at a 1.5 mL/min flow rate.

### RESULTS AND DISCUSSION

Low molecular weight oligomers were obtained at monomer concentrations below ca. 0.4 M in neopentane, 3-methylpentane, and 2,2- and 2,3-dimethylbutanes at 0 °C under rigorously dry conditions. The yield of oligomers was much smaller in hexane than in the branched hydrocarbons. Such a difference between the branched and linear hydrocarbons may arise from the free ion yields in the solvents.<sup>(4)</sup> The yields of the oligomers in the branched hydrocarbons are listed in Table 1. The  $G(-m)$  values are in the range from 14 to 250 at the monomer concentrations examined. They decrease with decreasing monomer concentration.

Table 1. The radiation-induced oligomerization of  $\alpha$ -methylstyrene in hydrocarbon solutions at 0°C\*

Solvent	Monomer concn., M	Conversion %	G(-m) $\times 10^{-2}$
Neopentane	0.39	21	2.5
	0.30	14	1.3
	0.20	17	1.0
	0.17	14	0.76
	0.12	18	0.63
	0.07	29	0.60
3-Methylpentane	0.36	11	1.1
	0.25	7.5	0.54
	0.21	6.7	0.40
	0.05	18	0.24
	0.02	26	0.14
2,2-Dimethylbutane	0.36	18	1.9
	0.21	12	0.79
2,3-Dimethylbutane	0.36	12	1.3
	0.20	10	0.59

\*The dose rate and irradiation time were  $5 \times 10^5$  rad/h and 1 h.

On the other hand, no detectable amount of oligomers was obtained when the solutions were degassed under vacuum without the rigorous drying. These results suggest that the oligomers are formed by a cationic chain reaction.

The molecular weight distribution curves for the oligomers produced in neopentane, 3-methylpentane, and 2,3-dimethylbutane

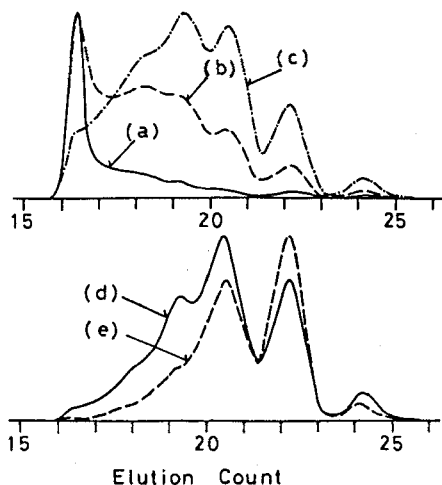


Fig.1. Molecular weight distribution curves for the oligomers produced in neopentane. Monomer concentrations: (a) 0.39 M; (b) 0.30 M; (c) 0.17 M; (d) 0.12 M; (e) 0.07 M.

are illustrated in Figures 1, 2, and 3, respectively. The oligomers produced in 2,2-dimethylbutane showed similar molecular weight distributions as those in 2,3-dimethylbutane at the same monomer concentration. The average molecular weights of the oligomers decreases with decreasing monomer concentration without change in position of each peak.

As reported earlier,<sup>(3)</sup> the average molecular weight of the oligomers produced in bulk at high temperature decreases with increasing temperature. In Figure 4, the molecular weight distribution curve for the oligomers produced at 0.02 M in 3-methylpentane is compared with that for the oligomers produced in bulk at 84 C (dotted line); their average molecular weights are comparable. For the oligomers produced in bulk at high

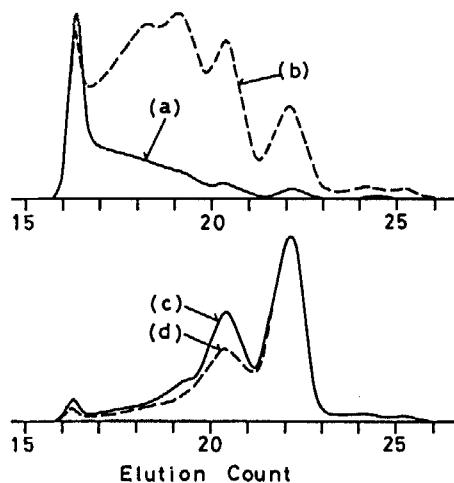


Fig.2. Molecular weight distribution curves for the oligomers produced in 3-methylpentane. Monomer concentrations: (a) 0.36 M; (b) 0.25 M; (c) 0.05 M; (d) 0.02 M.

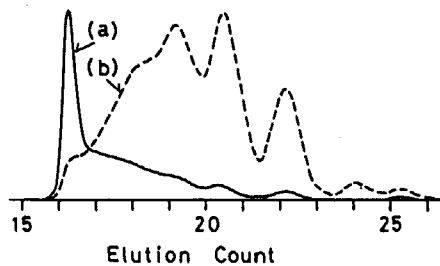


Fig.3. Molecular weight distribution curves for the oligomers produced in 2,3-dimethylbutane. Monomer concentrations: (a) 0.36 M; (b) 0.20 M.

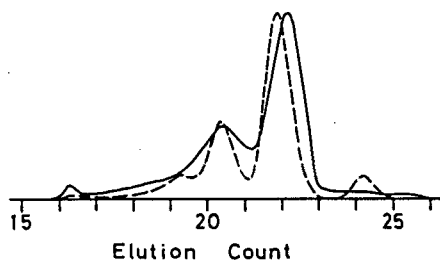


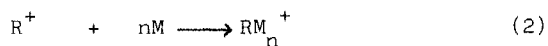
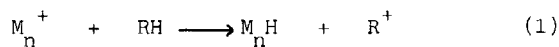
Fig.4. Comparison of the molecular weight distribution curves for the oligomers produced at 0.02 M in 3-methylpentane and at 84 C in bulk (dotted line).

temperature, the peaks at elution counts of 24.3, 22.0, 20.5, and 19.3 correspond to dimer, trimer, tetramer, and pentamer, respectively, and the peak at 16.2 counts includes higher polymers. These oligomers have been suggested to have substituted phenylindan end groups. A comparison of the distribution curves in Fig.4 shows that the main peaks at around 20 counts slightly differ from one another in position and that each peak for the 3-methylpentane system is broader than that for the bulk system. The positions and broadness of the peaks are similar for the oligomers produced in the hydrocarbon solutions as seen in Figs. 1-3. These results indicate that the product formation in the hydrocarbon solutions differs from that in bulk.

The mixtures of the oligomers produced in 3-methylpentane were submitted to  $^1\text{H}$ -NMR spectrometry, and the intensity ratios of the aliphatic protons to the aromatic protons,  $R_{\text{H}}$ , were determined. No olefinic proton was detected. The  $R_{\text{H}}$  values were 1.2, 1.5, and 2.0 for the oligomers produced at 0.25, 0.05, and 0.02 M, respectively. The value increases with decreasing monomer



concentration, i.e., with decreasing average molecular weight of the oligomers. Similar result was obtained for the oligomers produced in neopentane. For the oligomers produced in bulk at 84 C, the  $R_H$  value was 1.0, which is close to the calculated value, 1.1, for the main product, trimer. These results suggest that the oligomers produced in the hydrocarbon solutions contain the alkyl groups derived from the solvent molecules. The formation of the oligomers can be explained by the chain transfer to the solvents.



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