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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kubota, H. , Kabanov, V. Ya. , Squire, D. R. and Stannett, V.(1978) 'Radiation-Induced Polymerization of Ethyl Vinyl Ether in n-Pentane and Neopentane', Journal of Macromolecular Science, Part A, 12: 9, 1299 — 1305

To link to this Article: DOI: 10.1080/00222337808063193

URL: http://dx.doi.org/10.1080/00222337808063193

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J. MACROMOL. SCI.-CHEM., A12(9), pp. 1299-1305 (1978)

Radiation-Induced Polymerization of Ethyl Vinyl Ether in n-Pentane and Neopentane

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ABSTRACT

The radiation-induced polymerization of ethyl vinyl ether was studied in n-pentane and neopentane solutions under super-dry conditions. The free ion yields of these solvents are reported to be 0.16 and 1.0, respectively. The rate of polymerization in neopentane was about twice as fast as in n-pentane. The dose-rate dependence of the rate of polymerization was found to be nearly 0.50 in both solutions. It seems clear that the free solvent ions do, indeed contribute to the initiation. Regenerative chain transfer to monomer played a more important role in n-pentane than in neopentane as revealed by the molecular weight of the polymers.

INTRODUCTION

It is well known that vinyl ethers polymerize through a cationic mechanism by high-energy radiation. Studies [1-5] on radiation-induced ionic polymerization have almost all been conducted on bulk

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monomer systems where extremely dry conditions are required for the free cationic mechanism. Radiation-induced polymerization in solution systems [6] is more complex than bulk polymerization due to the contribution of the ions formed by radiolysis of the solvent to both the initiation and termination processes.

In this paper the radiation-induced polymerization of ethyl vinyl ether (EVE) was investigated in two similar solvents but with different free ion yields [7] in order to further clarify the nature of the solution polymerization. Neopentane was chosen as one of the solvents because of its high free ion yield, of about 1.0; the other was n-pentane, whose free ion yield is about 0.16.

EXPERIMENTAL

EVE was dried and purified by a technique described previously [4, 8]. n-Pentane was refluxed over sodium metal for 24 hr and the middle fraction collected. Neopentane of greater than 99.0% purity was used without further purification.

The monomer and solvent were super-dried separately by the sodium mirror method. The concentration of the monomer was kept at a constant volume of 50% in all solutions. The sample ampoules were all prepared according to the procedure reported by Goineau et al. [4].

Irradiation was carried out at 30°C in a cobalt-60 γ-ray source. Dose rates of 36.7, 49.4, and 70.6 rad/sec were determined by Fricke dosimetry.

The number-average molecular weights were determined with a Hewlett-Packard vapor-pressure osmometer in toluene at 37°C. Viscosity measurements were carried out in benzene solution at 30°C, and the weight-average molecular weights were calculated according to an equation developed for methyl vinyl ether [9].

RESULTS AND DISCUSSION

Table 1 shows the rates of polymerization in n-pentane and neopentane solutions. Higher rates of polymerization were obtained for neopentane solution at each dose rate, and the rate of polymerization was higher in the solvent with the higher free ion yield. The dose-rate dependence of the rate of polymerization was close to 0.5 in both n-pentane and neopentane solutions, as shown in Fig. 1. The ratio of the rates of polymerization in neopentane and n-pentane was found to be 1.8. The square root of the estimated free ion yields in both solvents, respectively, is estimated at about 1.9. It seems clear

TABLE 1. Rate of Polymerization in the Radiation-Induced Polymerization of EVE in n-Pentane and Neopentane Solutions

Dose rate (rad/sec)	R_p (mole/liter-sec)		R_p (neopentane) / R_p (n-pentane)
	n-Pentane	Neopentane	
36.7	1.7×10^{-5}	3.1×10^{-5}	1.82
49.4	1.9×10^{-5}	3.4×10^{-5}	1.79
70.6	2.5×10^{-5}	4.4×10^{-5}	1.76

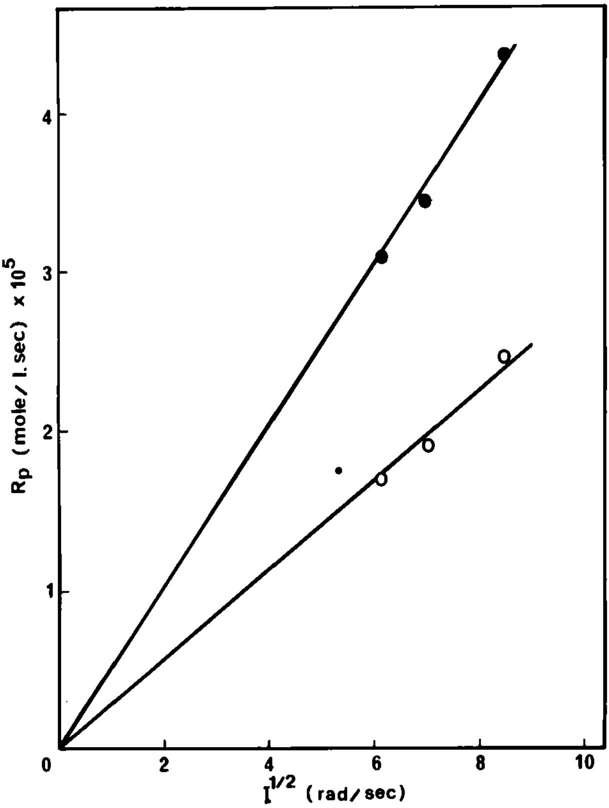

FIG. 1. Effect of dose rate on rate of radiation-induced polymerization of EVE at 30°C, 50% solution by volume: (●) in neopentane; (○) in n-pentane.

that the increased free ion yield does indeed contribute proportionally to the rate of polymerization.

Duplessis et al. [6] modified the model of Williams [10] for the ionic solution polymerization and derived the following kinetic scheme on the rate of polymerization:

$$R_p = R_i k_{pm}[M]/\{(R_i K_t)^{0.5} + K_{tx}[X] + K_{ts}[S]\}$$

where

$$R_i = R_{im} + R_{is}$$

R_{im} and R_{is} are the rates of free ion formation for monomer and solvent, respectively, [M], [X], and [S] are the concentrations of monomer, impurities, and solvent, respectively; k_{pm} is the rate constant for propagation, K_t is the termination rate constant for the recombination of the growing cations and the negative species originated from monomer, K_{tx} is the rate constant for termination with impurities, and K_{ts} is the rate constant for chain transfer to solvent. The extra termination term $K_{ts}[S]$ is involved only when the solvent transferred ions are too stable to reinitiate polymerization.

In the case which the termination with impurities and the chain transfer to solvent do not play an important role in the rate of polymerization $K_{tx}[X] + K_{ts}[S] \ll (R_i K_t)^{0.5}$; the dose-rate dependence of R_p has a value of 0.5. In the contrary case, R_p is predicted to be proportional to the first power of the dose rate. Although the values obtained experimentally in n-pentane and neopentane solutions deviate slightly from the square root dependence, the termination with impurities and the chain transfer to solvent seem to be of no great significance in the rates of this solution polymerization. It is curious, however, that the bulk rates are about five times higher than in neopentane solution. There appears to be no obvious explanation for this observation.

The number-average molecular weights and G(m) values are shown in Table 2. Both the molecular weight and G(m) values were found to be higher in neopentane solution. The molecular weights in both solutions were lower compared with those obtained in bulk EVE system which were found to be about 40,000 under comparable conditions. Table 2 also includes the value of $G(m)/\overline{DP}_n$, which is a

TABLE 2. Number-Average Molecular Weight and G(m) Value in the Radiation-Induced Polymerization of EVE in n-Pentane and Neopentane Solutions

Dose rate (rad/sec)[a]	$\overline{M}_n$		G(m)		G(m)/$\overline{DP}_n$	
	n-Pentane	Neopentane	n-Pentane	Neopentane	n-Pentane	Neopentane
36.7	5900	9940	575	1139	7.0	8.3
70.6	4750	7060	463	807	7.0	8.2

[a] Total dose: 6.2 Mrad.

measure of the relative importance of the propagation reaction and the regenerative chain transfer to monomer. The values were 7-8 in both n-pentane and neopentane solutions, indicating the existence of the chain transfer process. The same phenomenon of chain transfer to monomer was observed in polymerization of EVE initiated in methylene chloride solution by stable carbonium ion salts [8, 11]. If the free ion yield of EVE is assumed to be about 0.14, which is the value reported for isobutyl vinyl ether [2], the average number of regenerative chain transfer steps N occurring during the kinetic lifetime of each carbenium ion can be estimated according to the equation [5]:

$$N = \frac{G(m)/\overline{DPn}}{G_i} - 1;$$

where $G_i \simeq \frac{1}{2}(G_{iM} + G_{iS})$, G_{iM} and G_{iS} are the free ion yields for monomer and solvent, respectively. The values calculated were 45.7 and 13.5 for n-pentane and neopentane solutions, respectively, at a total dose of 6.2 Mrad. There are clearly more chain transfer steps during the kinetic lifetime of each propagating carbenium ion in n-pentane solution. This is in keeping with the structure of the two solvents. The differences of molecular weight in the two solutions presumably originates from the extent of chain transfer to monomer.

Finally, it is worthwhile to know the ratios $\overline{M}_w/\overline{M}_n$; these were found to be 1.9 and 2.3 for the polymers obtained in n-pentane and neopentane solutions, respectively. The chain lengths in both the solutions appear to follow the most probable distribution [12], where the ratio is expected to be 2.0 for termination by chain transfer.

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Accepted by editor May 30, 1978
Received for publication June 6, 1978