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Radiation-Induced Copolymerization of Ethyl Vinyl Ether with Dibutyl Maleate

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ABSTRACT

The radiation-induced copolymerization of ethyl vinyl ether with dibutyl maleate was investigated over a wide range of comonomer compositions, dose rates, and in the temperature range from -25 to 75°C. Both the rates of copolymerization and the molecular weights of the resulting copolymers were found to depend strongly on the initial comonomer composition, both reaching a maximum value at an equimolar comonomer composition. A copolymer was obtained in which the comonomers alternate with regularity along the polymer chain over the entire range of comonomer compositions investigated. The monomer reactivity ratios were determined and found to be practically zero. The apparent activation energy was found to change at 35° C, the boiling point of the ethyl vinyl ether, from a value of 10.48 kJ/mole to a value of 18.86 kJ/mole above this temperature. This phase change also resulted in a marked decrease in the molecular weights of the copolymers formed above 35°C. The dose-rate dependence of the rate of copolymerization was found to be 0.70 over the dose-rate range from 0.02 to 2.4 Mrad/hr. Scavenger studies indicate that a free-radical mechanism prevails over all the temperature and dose-rate ranges investigated.

INTRODUCTION

Investigations carried out on the homopolymerization and copolymerization of ethyl vinyl ether indicate that this monomer has an exceptionally low tendency to react with itself in free-radical polymerization processes [1-4]. This tendency results in the formation of copolymers with a marked alternating structure [3]. Correspondingly, the radiation-induced copolymerization of the unsaturated alkyl esters of maleic acid indicates that these monomers are very difficult to homopolymerize through radiation-initiation, and form completely alternating copolymers with vinyl acetate [5].

As the copolymers of both the vinyl ethers and the unsaturated alkyl esters of maleic acid are known to be industrially important in the field of adhesives and coatings, this investigation was carried out in order to determine some of the basic aspects of the copolymerization of ethyl vinyl ether with dibutyl maleate, in an attempt to synthesize these important compounds by means of ionizing radiation.

EXPERIMENTAL

Materials and Procedure

Both monomers were obtained from Fluka Chemicals. Ethyl vinyl ether (EVE) had an indicated purity of 98% (GC), and the stabilizer (potassium hydroxide, 0.1%) was removed by vacuum distillation of the monomer immediately before use. Dibutyl maleate (DBM) was used from the bottle after gas-chromatographic analyses had indicated a purity in excess of 98%.

Comonomer mixtures were prepared by pipetting the appropriate volumes of the monomers into glass ampoules, degassing of the mixtures on a vacuum line by repeated processes of freezing and thawing, and subsequent sealing of the ampoules.

The irradiations were carried out under temperature control in both a nominal 50 kCi Gammabeam-650 irradiator and a nominal 11kCi Gammacell irradiator, both supplied by Atomic Energy of Canada Limited.

The copolymers which formed were dissolved in acetone, precipitated in excess methanol, and dried in a vacuum oven at 60° C to constant weight.

Dose rates were determined by Fricke dosimetry.

Analyses of the Copolymers

The infrared spectra of the copolymers and the two homopolymers were obtained from thin films of the copolymers cast from solutions in acetone onto KBr disks.

Viscosity measurements were carried out (using chloroform as solvent for the copolymers) by means of a constant-temperature bath at 30° C and an Ubbelohde viscometer. Number-average molecular weights were determined by membrane osmometry, chloroform being used as solvent for the copolymers at 30° C.

The molar ratios of the two monomers present in the copolymers were determined from elemental analyses of the copolymers for carbon and hydrogen.

Thermal analyses of the copolymers and homopolymers were carried out by means of differential-scanning calorimetry (DSC).

RESULTS AND DISCUSSION

Nature of the Copolymer

The radiation-induced copolymerization of ethyl vinyl ether with dibutyl maleate results in a crystal-clear copolymer with excellent adhesive properties and holds promise as a clear coating material at high molecular weights.

Nature of the Propagating Species

As no special care was taken in drying the monomers for this investigation, the possibility that ionic polymerization mechanisms can play a significant role in the overall copolymerization process is very limited [4].

It was observed (Fig. 1) that a definite change in apparent activation energy for the copolymerization process takes place at about 35° C, and that this is accompanied by a corresponding marked drop in the molecular weight of the copolymer formed. It was furthermore observed that the molecular weight of the copolymer increases with an increase in dose rate between 0.1 and 1.0 Mrad/hr (see Fig. 2).

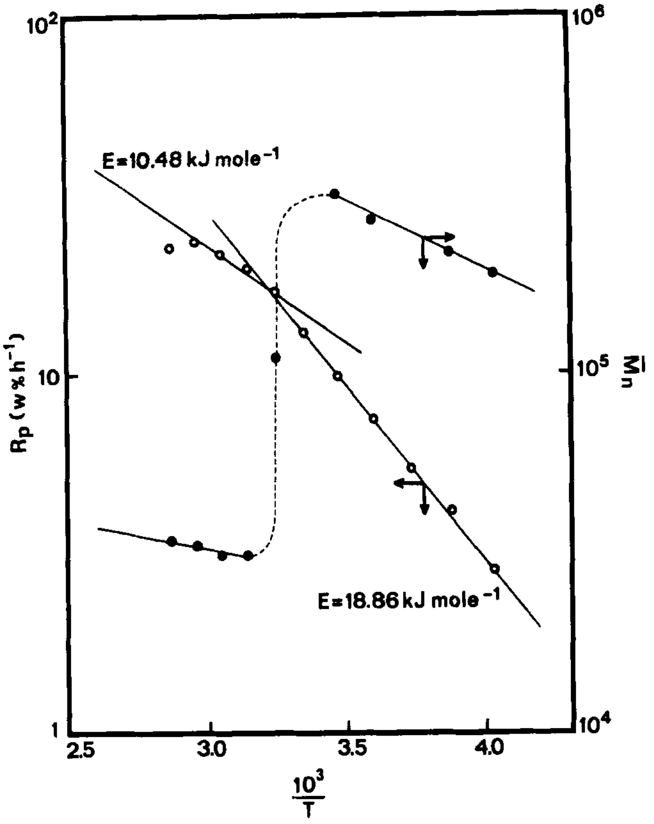

FIG. 1. Influence of irradiation temperature on (●) the rate of copolymerization and (○) the number-average molecular weight of the copolymer formed at a dose rate of 0.18 Mrad/hr.

In order to determine whether these phenomena were the result of changes in the nature of the propagating species with a change in temperature or dose rate, the influence of both free-radical and ionic scavengers was investigated well above and well below the temperatures and dose rates at which the changes take place.

As follows from Table 1, ammonia has no marked effect on the rates of copolymerization over the entire temperature and dose-rate ranges investigated, thus excluding an ionic mechanism. The

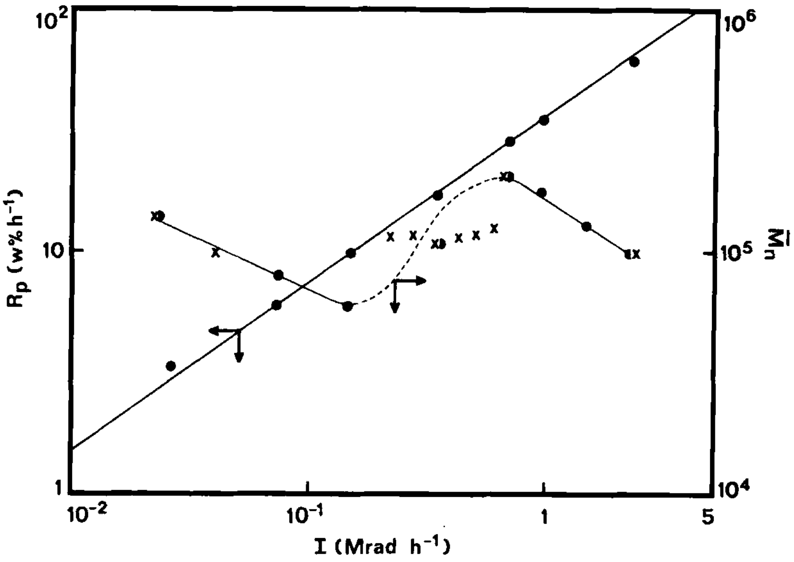

FIG. 2. Influence of the dose rate on (●) the rate of copolymerization and (×) the number-average molecular weight of the copolymer formed at an irradiation temperature of 25° C.

TABLE 1. Influence of Scavengers on the Rates of Copolymerization at Different Dose Rates and Temperatures

		Rate of copolymerization (%/hr)			
Additive	Concentration (w/w)	0.184 Mrad/hr, 55° C	0.023 Mrad/hr, 25° C	0.351 Mrad/hr, 25° C	2.304 Mrad/hr, 25° C
None	-	21.8	2.9	17.6	65.6
Benzoquinone	1.0	0	0	0	0
Oxygen	saturated	0.4	0.1	0.3	0.4
Ammonia	saturated	20.8	2.7	16.8	64.5

free-radical scavengers, benzoquinone and oxygen, on the other hand, markedly lower the rates of copolymerization over the temperature and dose-rate ranges investigated.

From these results we conclude that the radiation-induced copolymerization of ethyl vinyl ether with dibutyl maleate proceeds by means of a free-radical process over the temperature and dose-rate ranges investigated.

Composition of Copolymers and Monomer Feed

The chain-propagating reactions that may occur when the two monomers EVE and DBM are present, can be written as shown in Eqs. (1)-(4), where M_1 represents EVE and M_2 is DBM

$$-M_1^{\cdot} + M_1 \xrightarrow{k_{11}} -M_1^{\cdot} \quad (1)$$

$$-M_1^{\cdot} + M_2 \xrightarrow{k_{12}} -M_2^{\cdot} \quad (2)$$

$$-M_2^{\cdot} + M_1 \xrightarrow{k_{21}} -M_1^{\cdot} \quad (3)$$

$$-M_2^{\cdot} + M_2 \xrightarrow{k_{22}} -M_2^{\cdot} \quad (4)$$

The first subscript attached to the propagation-rate constants refers to the reacting radical, and the second to the monomer.

The composition of the copolymer as a function of the monomer-mixture composition at 25°C is shown in Fig. 3. It follows from these results that the composition of the copolymer remains constant at an equimolar composition for all monomer compositions, and that the two monomer units tend to alternate regularly along the polymer chain. This suggests that both monomer-reactivity ratios should be small, i.e., $r_1r_2 \ll 1$.

Using the Alfrey-Price treatment [6], a reasonable approximation of the monomer reactivity ratios may be calculated for the copolymerization of EVE and DBM. In Table 2 these values are compared with the values calculated from experimental data by using three different methods [7-10].

Referring to the propagating reactions (1)-(4), it follows that for this copolymer system, the cross-propagating reactions play the most important role in the determination of the arrangement of the

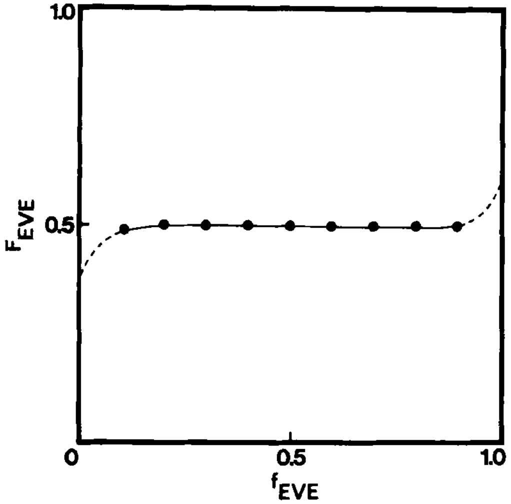

FIG. 3. Composition of the copolymer as a function of the initial comonomer composition at 25°C.

TABLE 2. Monomer Reactivity Ratios for the Radiation Copolymerization of Ethyl Vinyl Ether (M_1) with Dibutyl Maleate (M_2)

Method	r_1	r_2
Alfrey-Price	0.030	0.016
Fineman- Ross	0.000	0.005
Tosi	0.000	0.004
Braun- Brendlein-Mott	0.003	0.005

monomer units along the copolymer chain. This is normally the case where the rates of homopolymerization of both comonomers are low. It also leads to the formation of a copolymer where the monomer units tend to alternate fairly regularly along the polymer chain, which is in good agreement with the experimental data presented in Fig. 3.

Rates of Copolymerization

The relation between the percentage conversion of monomers at an initial equimolar composition of the comonomers and the irradiation

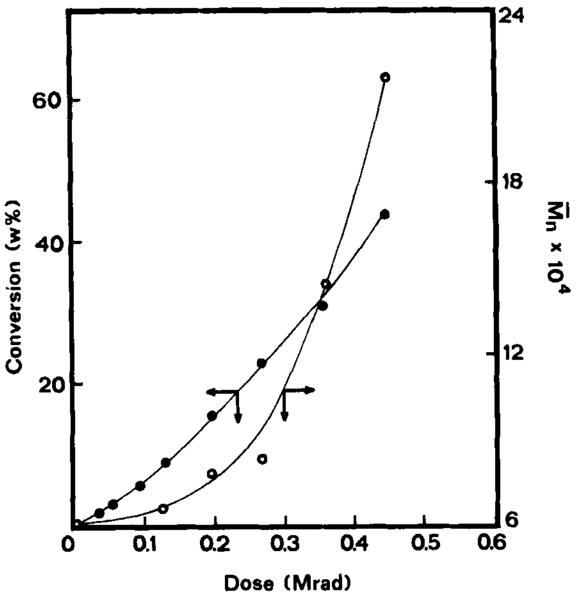

FIG. 4. Plots of (●) percentage monomer conversion to polymer and (○) the number-average molecular weight of the copolymer as functions of the irradiation dose at a dose rate of 0.18 Mrad/hr and an irradiation temperature of 25°C.

dose at a dose rate of 0.18 Mrad/hr and an irradiation temperature of 25°C is shown in Fig. 4. The conversion increases linearly without any induction period or acceleration phenomenon up to about 44%.

The rate of copolymerization at 25°C and a dose rate of 0.18 Mrad/hr as a function of the mole fraction of EVE in the initial comonomer mixture is shown in Fig. 5. It is apparent that the rate of copolymerization reaches a maximum value at an equimolar comonomer mixture. This is in good agreement with the expectations for a copolymer in which the monomers alternate regularly along the chain, and where the cross-propagating reactions take place almost exclusively.

Effect of Irradiation Temperature on Rate of Copolymerization

The effect of the irradiation temperature on the rate of copolymerization was investigated over the temperature range -25 to 75°C. An

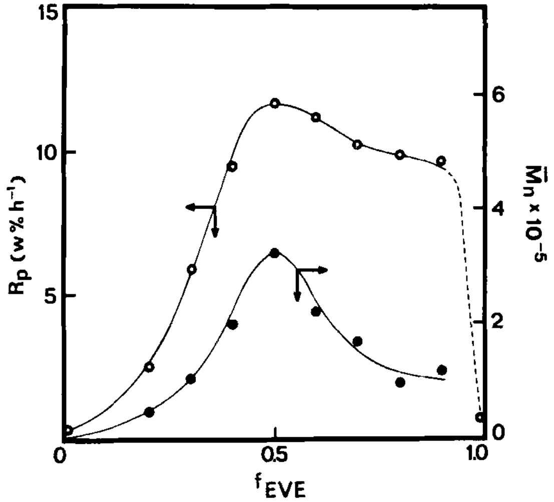

FIG. 5. Plots of (○) the rate of copolymerization and (●) the number-average molecular weight of the copolymer as functions of the initial comonomer composition at a dose rate of 0.18 Mrad/hr and an irradiation temperature of 25° C.

Arrhenius plot of the results at a dose rate of 0.18 Mrad/hr and an equimolar comonomer composition is given in Fig. 1. The apparent activation energy increases from a value of 10.48 kJ/mole at a temperature of 35° C to a value of 18.86 kJ/mole above this temperature. This change in activation energy is not the result of a change in the nature of the propagating species (as follows from Table 1), but can rather be related to a phase change that takes place in the case of EVE boiling at 35° C, thus resulting in the increase in activation energy.

Effect of Dose Rate on the Rate of Copolymerization

The dose-rate dependence of the rate of copolymerization at 25° C and an initial equimolar comonomer composition is shown in Fig. 2. It follows from Fig. 2 that the rate of copolymerization exhibits a dose-rate dependence of 0.70 in the range from 0.02 to 2.40 Mrad/hr—a value which suggests that bimolecular termination processes play the predominant role in the copolymerization.

Molecular Weight of Copolymer

Molecular weights of the copolymers were determined by means of membrane osmometry, and the corresponding intrinsic viscosities for the copolymer solutions in chloroform at 30° C were also obtained. The constants for the Mark-Houwink equation, giving the relationship between the intrinsic viscosity and the number-average molecular weight were found to be as follows: $a = 0.14$; $K = 7.80 \times 10^{-2}$.

As follows from Fig. 4, the number-average molecular weight of the copolymer increases almost exponentially with an increase in irradiation dose or percentage conversion. From Fig. 5 it furthermore follows that the number-average molecular weight of the copolymer is strongly dependent on the initial comonomer composition, reaching a maximum value at an equimolar comonomer composition. This is in good agreement with the expectations for a copolymerization process in which the comonomers alternate regularly along the chain and where the cross-propagating reactions take place almost exclusively.

As follows from Fig. 1, the number-average molecular weight of the copolymer is strongly dependent on the irradiation temperature. At 35°C the molecular weight undergoes a sharp drop with a further increase in temperature, a phenomenon which can be ascribed to a change in phase of the EVE, as discussed earlier.

It was found that the number-average molecular weight of the copolymer exhibits a dose-rate dependence of about -0.60 in the range 0.02 to 2.40 Mrad/hr. Between the dose-rate values of 0.15 to 0.70 Mrad/hr, however, the number-average molecular weight undergoes a marked increase with an increase in dose rate. As this is not the result of a change in the nature of the propagating species (as follows from Table 1), no explanation can at present be presented for this phenomenon.

Infrared Spectrum of the Copolymer

A comparison of the infrared spectra of the copolymer and homopolymers does not reveal sufficient differences in the fingerprint region to enable one to conclude with certainty that the polymeric products are indeed copolymers and not mixtures of the respective homopolymers. However, differential-scanning calorimetry demonstrates conclusively that the possibilities of the production of mixtures of homopolymers or block copolymers can be excluded.

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