

Radiation-Induced Copolymerization of Isobutyl Vinyl Ether with Trichloroethylene

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Synopsis

The radiation-induced copolymerization of isobutyl vinyl ether with trichloroethylene was investigated in the temperature range from -50°C to 100°C over a wide range of comonomer compositions. A copolymer was obtained in which the monomers alternate with regularity along the polymer chain over essentially the entire range of comonomer compositions. Both the rate of copolymerization and the number-average molecular weight of the resulting copolymer were found to depend strongly on the initial comonomer composition. The monomer reactivity ratios were determined and correspond well with calculated values. An apparent activation energy of 3.2 kcal/mole was obtained for the copolymerization process which exhibits a dose rate dependence of 0.72. The number-average molecular weight was found to be strongly dependent on the irradiation temperature, reaching a maximum value at 5°C .

INTRODUCTION

Considerable interest has been shown in the radiation-induced homopolymerizations of the vinyl ethers during the last few years.¹⁻⁴ Most of these studies were aimed at the radiation-induced free-cationic polymerizations of these monomers and were carried out under "super dry" conditions which led to very high rates of polymerization. A limited number of investigations were carried out on the radiation copolymerizations of the vinyl ethers with other monomers, namely, the copolymerization of *n*-butyl vinyl ether with tetrafluoroethylene,⁵ that of ethyl vinyl ether with chlorotrifluoroethylene,⁶ and that of isobutyl vinyl ether with styrene.⁷ The first two of these radiation copolymerizations were characterized by the alternation of the two comonomers with near perfect regularity along the polymer chain.

No attempt has been made either to homopolymerize or copolymerize trichloroethylene by means of radiation. Since trichloroethylene is a relatively inexpensive monomer, we decided to investigate the radiation copolymerization of this monomer with isobutyl vinyl ether, the latter being one of the most reactive members of the vinyl ether series towards radiation polymerization,⁸ in an attempt to synthesize a new and potentially useful elastomer.

EXPERIMENTAL

Materials and Procedure

Isobutyl vinyl ether (Fluka Chemicals, 98%) and trichloroethylene (May and Baker Chemicals, 99%) were purified by vacuum distillation and dried with calcium chloride. In some experiments the monomers were dried on Davison molecular sieves obtained from Fisher Scientific Company and were of the Type 3A (Grade 564), 8–12 mesh with an effective pore size of 3 Å. The decision to use these sieves was based on earlier work.⁹

Comonomer mixtures were prepared as follows. The monomers were transferred *in vacuo* from reservoirs to calibrated glass tubes. The appropriate volumes of the monomers were then transferred from these tubes at 25°C to 20 ml glass ampoules which were subsequently sealed.

The copolymer that formed was dissolved in acetone, filtered, and precipitated in methanol before drying for 24 hr in a vacuum oven at 70°C to constant weight.

The irradiations were carried out in a nominal 50 kCi Gammabeam 650 irradiator as supplied by Atomic Energy of Canada Ltd. Dose rates were determined by Fricke dosimetry.*

Analyses of the Copolymer

The molar ratio of the two monomers present in the copolymer was determined from elemental analyses of the copolymer for chlorine, carbon and hydrogen.

The infrared spectra of the copolymers were obtained from thin films of the copolymer cast onto KBr disks from solutions of the copolymer in chloroform.

The number-average molecular weights of the copolymers were determined by vapor-pressure osmometry with toluene as solvent. Thermal studies were carried out by using a Perkin-Elmer differential scanning calorimeter (Type DSC-IB).

RESULTS AND DISCUSSION

Nature of the Propagating Species

According to the classification of Schildknecht,¹⁰ the vinyl ethers display a marked preference for polymerization by cationic catalysts. Bonin et al.¹¹ established that ions play the predominant role as chain intermediates in the radiation-induced polymerization of isobutyl vinyl ether (IBVE). Williams¹² indicated, however, that such radiation-induced cationic polymerizations are extremely sensitive to trace amounts of impurities, such as water, and with such impurities present the ionic contribution to the polymerization mechanism can be completely eliminated.

* The various dose rates utilized for the different sections of the study were necessitated by practical considerations in terms of available radiation-source time.

TABLE I
Influence of Scavengers on the Rate of Copolymerization at 25°C^a

Additive		
Type	Concn, % (v/v)	R_p , wt-%/hr
None	—	5.80
CH ₂ Cl ₂	50	5.75
NH ₃	5	5.52
H ₂ O	5	5.56
Benzoquinone	1	0.58
O ₂	Saturated	1.10

^a Equimolar monomer composition; dose rate 0.5 Mrad/hr.

The halogenated vinyls, on the other hand, have a preference for polymerization through a free-radical mechanism.¹³ Taking into account that neither IBVE nor trichloroethylene (TCE) was dried thoroughly in the present investigation, one would expect free radicals to be the predominating chain intermediates in the copolymerization of IBVE and TCE.

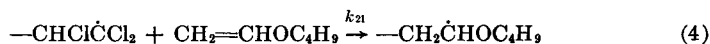
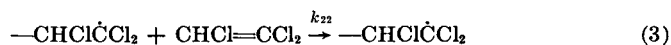
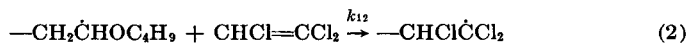
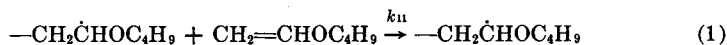
As follows from Table I, neither ammonia nor water has any marked effect on the rate of copolymerization, thus excluding an ionic mechanism. Methylene chloride, which normally enhances the rate of ionic polymerization in a "wet" system⁴ also has little effect on the rate of copolymerization. The free-radical scavengers benzoquinone and oxygen, on the other hand, markedly lower the rate of copolymerization.

Gel-permeation chromatograms indicate only one defined peak in the molecular weight distribution over a wide range of temperatures. This further supports the fact that only one copolymerization mechanism is operating, since, when both free-radical and ionic mechanisms prevail, the molecular weight distribution of the resulting polymer usually exhibits a bimodal distribution.¹⁴ Furthermore, the overall activation energy of this copolymerization has a value of 3.2 kcal/mole, a value which is in good agreement with that normally found for free-radical mechanisms.

From these results we conclude that for the present investigation the copolymerization of IBVE and TCE proceeds by means of a free radical process.

Composition of Copolymer and Monomer Feed

The chain-propagating reactions that may occur when the two monomers, isobutyl vinyl ether (IBVE) and trichloroethylene (TCE), are present, can be written as shown in eqs. (1)–(4).



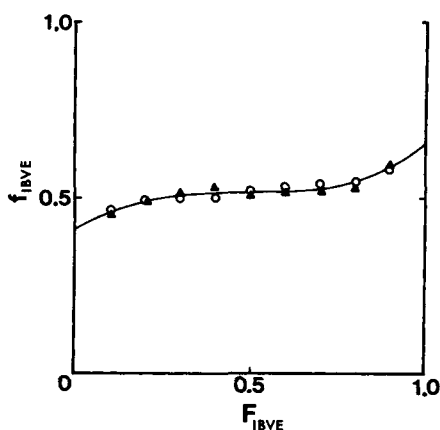


Fig. 1. Mole fraction of IBVE in copolymer as a function of mole fraction IBVE in comonomer mixture at 25°C.

The first subscript attached to the propagating rate constants refers to the reacting radical, and the second to the monomer. The monomer reactivity ratios are defined by

$$r_1 = k_{11}/k_{12}$$

and

$$r_2 = k_{22}/k_{21}$$

The monomer reactivity ratios thus give the tendency for a given radical to add its own monomer to the tendency to add to the other monomer.

The composition of the copolymer as a function of the monomer mixture composition at 25°C is shown in Figure 1. It follows from these results that the composition of the copolymer remains fairly constant at a molar fraction of nearly 0.5 for all monomer compositions, and that the two monomer units tend to alternate regularly along the polymer chain. This regular alternation of the two monomer units suggest that both monomer reactivity ratios should be small, i.e., $r_1 r_2 \ll 1$.

Using the Alfrey-Price treatment,¹⁵ a reasonable approximation of the monomer reactivity ratios may be calculated for the copolymerization of IBVE and TCE. From the listed values according to Young,¹⁶ the calculated values are $r_1 = 0.002$, $r_2 = 0.001$.

By using the graphical method of Fineman-Ross,¹⁷ the monomer reactivity ratios may be calculated from the experimental data, and are found to be $r_1 = 0.045$, $r_2 \sim 0$. These values correspond fairly well with the calculated values obtained from the copolymerization parameters.

Referring to the propagating reactions (1)–(4), it follows that in this system the cross-propagating reactions play the most important role in the determination of the arrangement of the monomer units along the polymer chain. This leads to the formation of a copolymer where the monomer

units tend to alternate fairly regularly along the polymer chain, in good agreement with the experimental data in Figure 1.

The tendency for monomers to alternate during copolymerization closely parallels the order of the tendency of substituents around the double bond to withdraw from or donate electrons to the double bond. In the case of IBVE the butoxyl group has an electron-donating effect on the double bond, whereas in the case of TCE the chlorine atoms have a strongly electron-withdrawing effect on the double bond. These effects probably exert a strong influence on the tendency towards alternation in the copolymerization of these two monomers.

Rate of Copolymerization

The relation between the per cent conversion of monomers at an initial equimolar comonomer composition, and irradiation time at a dose rate of 1 Mrad/hr and an irradiation temperature of 25°C is shown in Figure 2. The conversion increases linearly, without any induction period or accelera-

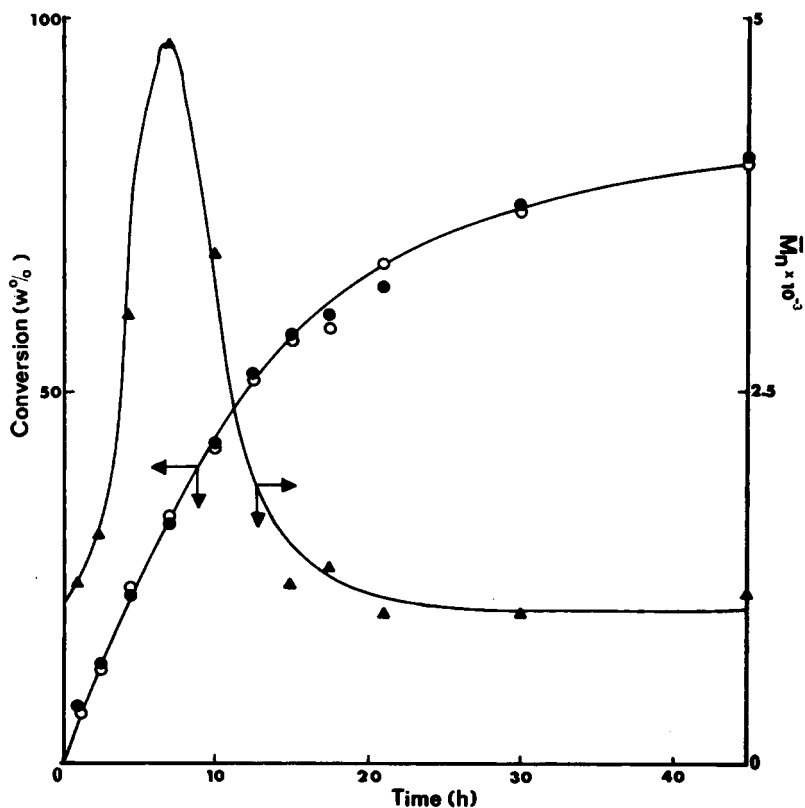


Fig. 2. Monomer conversion and number-average molecular weight of copolymer formed at 25°C and a dose rate of 1 Mrad/hr as a function of the irradiation time at a mole fraction of 0.5 for IBVE in the comonomer mixture.

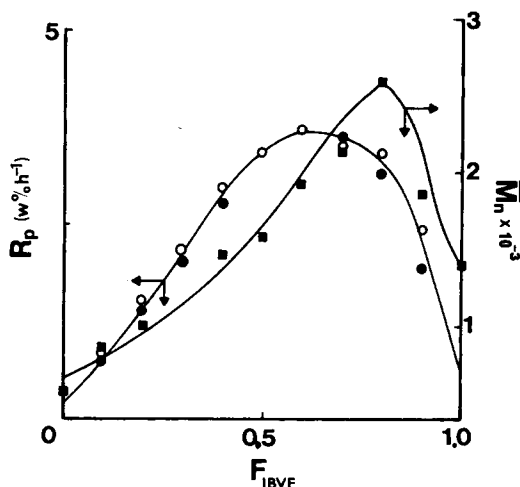


Fig. 3. Rate of copolymerization and number-average molecular weight of copolymer formed at 25°C and a dose rate of 0.5 Mrad/hr as a function of the mole fraction IBVE in the comonomer mixture.

tion phenomenon, up to about 60%, at which point the rate of conversion starts leveling off.

The number-average molecular weights of the copolymers obtained under the same experimental conditions are also shown in Figure 2 as a function of the irradiation time. It follows from this figure that the molecular weight increases sharply with irradiation time or conversion up to about 32% conversion. Beyond this point, the molecular weight starts dropping sharply with a further increase in dose. This remarkable change in molecular weight is probably the result of the radiation degradation of the copolymer which becomes more important than the chain propagation at conversions higher than about 32%. The fact that the resulting copolymer is highly soluble in the comonomer mixture will further contribute to the radiation degradation of the copolymer.

The rate of copolymerization at 25°C and a dose rate of 0.5 Mrad/hr as a function of the mole fraction of IBVE in the initial comonomer mixture, is shown in Figure 3. From Figure 3 it is apparent that the rate of copolymerization reaches a maximum value close to about an equimolar comonomer composition. This is in 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.

The number-average molecular weights of the copolymers obtained at 25°C and a dose rate of 0.5 Mrad/hr, are also given in Figure 3 as a function of the mole fraction of IBVE in the comonomer mixture. It is apparent from Figure 3 that the initial monomer composition has a remarkable influence on the molecular weight of the resulting copolymer. The trend of this curve corresponds fairly well to that of the rate of copolymerization.

The fact that the maximum molecular weights are obtained at comonomer compositions slightly higher than 0.5 for IBVE is probably the result of the increased chain transfer that can take place at higher concentrations of TCE, the latter acting as a fairly good chain-transfer agent.

Effect of Temperature on the Copolymerization

The effect of temperature on the rate of copolymerization and the molecular weight of the resulting copolymer were investigated in the temperature range from -50°C to 100°C . An Arrhenius plot of the results at a dose rate of 2 Mrad/hr and equimolar comonomer compositions is given in Figure 4. An apparent activation energy of 3.20 kcal/mole is obtained from Figure 4, a value which is consistent with a free-radical copolymerization process. There is no indication of a change in copolymerization mechanism over the entire temperature range investigated.

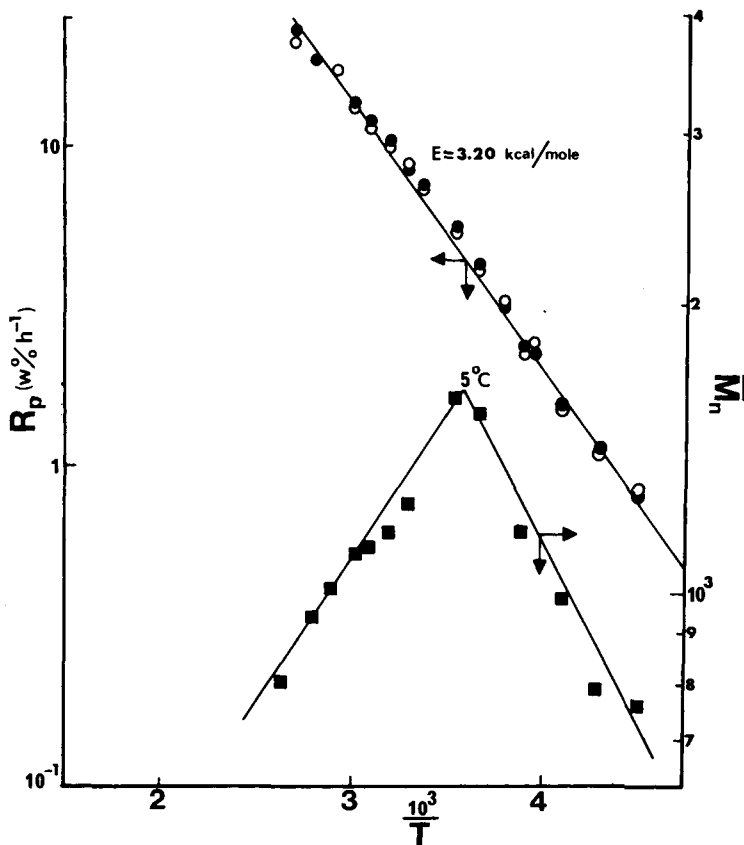


Fig. 4. Rate of copolymerization and number-average molecular weight of copolymer formed as a function of the irradiation temperature at a mole fraction of 0.5 for IBVE in the comonomer mixture and a dose rate of 2 Mrad/hr.

The number-average molecular weights of the copolymers formed are highly dependent on the copolymerization temperature as follows from Figure 4. With an increase in temperature from -50°C to about 5°C the molecular weight increases with an increase in temperature. Beyond 5°C the molecular weight drops sharply with increase in temperature. This phenomenon is probably attributable to the relative importance of chain-propagating and chain-transfer processes. Above 5°C regenerative chain-transfer processes to monomer apparently dominate chain propagation, resulting in a decrease in the molecular weight of the copolymer. This is in agreement with a similar effect observed in the homopolymerization of IBVE.⁴

Effect of Dose Rate on the Copolymerization

The dose-rate dependence of the rate of copolymerization at 25°C and an initial equimolar comonomer composition, is given in Figure 5. As follows from Figure 5, R_p exhibits a dose rate dependence of 0.72. This

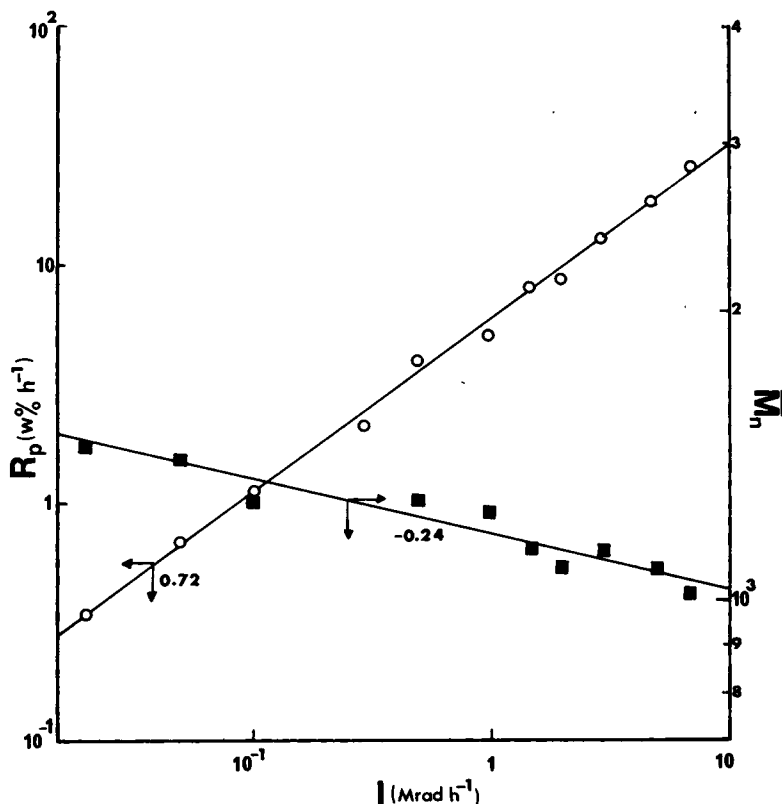


Fig. 5. Rate of copolymerization and number-average molecular weight of copolymer formed as a function of the dose rate at a mole fraction of 0.5 for IBVE in the comonomer mixture and an irradiation temperature of 25°C .

value suggests that both bimolecular and monomolecular termination processes play a role in the copolymerization.

It further follows from Figure 5 that the number-average molecular weight of the resulting copolymer decreases with an increase in dose rate, with a dose-rate dependence of -0.24 . This is in agreement with theoretical expectations.

Infrared Spectrum of the Copolymer

The infrared spectrum of the copolymer obtained from an equimolar comonomer composition at 25°C is shown in Figure 6, together with the spectra of poly(IBVE) and poly(TCE), the latter two homopolymers both being obtained through radiation polymerization.

It is evident from Figure 6 that the infrared spectrum of the copolymer (Fig. 6b) is quite different from that of both the homopolymers, poly(IBVE) (Fig. 6a) and poly(TCE) (Fig. 6c). In the spectrum of the copolymer there are two strong peaks at $2950 \pm 5 \text{ cm}^{-1}$ and $2880 \pm 5 \text{ cm}^{-1}$ which may be attributed to the symmetric and asymmetric vibrations of methylene groups in structures of the type $-\text{CHClCH}_2-$. The existence of these two peaks, arising from the vinyl group in IBVE, indicate the presence of this monomer in the polymer structure. This is further supported by the strong absorption at $1050\text{--}1125 \pm 5 \text{ cm}^{-1}$ resulting from the C-O stretching vibration in the ether group. The strong peak at $750 \pm 5 \text{ cm}^{-1}$ is ascribed to the

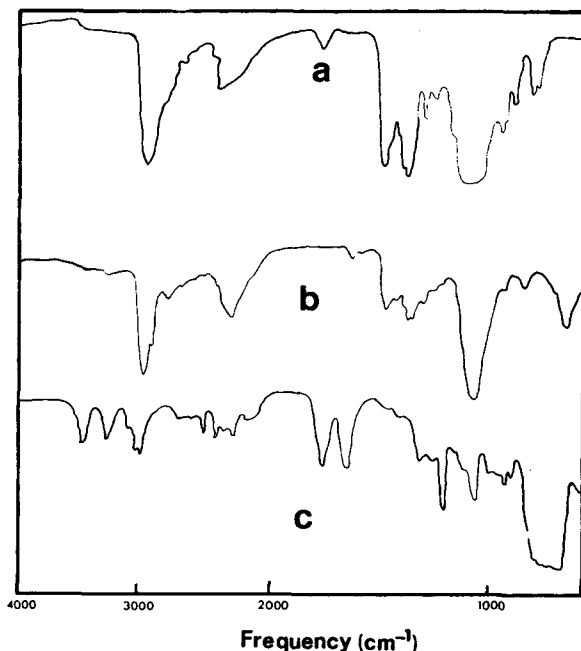


Fig. 6. Infrared spectra of: (a) poly(isobutyl vinyl ether); (b) poly(isobutyl vinyl ether-co-trichloroethylene); and (c) poly(trichloroethylene).

C-Cl stretching vibration from the TCE group in the copolymer, a peak which is completely absent in poly(IBVE).

Thermal studies on the copolymer by means of differential-scanning calorimetry indicated that a single polymer was formed, with no indication of the presence of two homopolymers.

These facts suggest that the alternative possibilities of the production of a mixture of homopolymers or a block copolymer can be excluded and that the copolymer always has a highly regular structure which is largely independent of the concentration of the comonomers in the monomer mixture.

Physical Properties of Copolymer

A hard and pale yellow elastomer that is soluble in most organic solvents is formed under optimum conditions, i.e., at an irradiation temperature of 5°C, mole fraction of IBVE in the comonomer mixture of 0.8, and monomer conversion of about 32%. Deviations from these conditions result in the formation of sticky copolymer of low molecular weight. Under optimum conditions the copolymer has a melting point of about 40°C.

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