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Cationic Polymerization of Isobutyl Vinyl Ether in Solution by Radiation

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ABSTRACT

The radiation-induced cationic polymerization of isobutyl vinyl ether in solutions of diethyl ether and methylene chloride was investigated under conditions where the monomer and solvents were dried with molecular sieves to high levels of dryness. The investigation covered the temperature range from -16 to 90°C, the dose-rate range from 10^{15} to 10^{20} eV/(g)(sec) (using both gamma rays and electrons), and the influence of diethyl ether and methylene chloride as solvents for the monomer.
For the solution of the monomer in diethyl ether, a very high overall activation energy of 29.7 kcal/mole was found, which decreased sharply to a value of 1.2 kcal/mole above 30°C. No such change was found for the monomer solution in methylene chloride.
The dose-rate dependence of the rate of polymerization for the monomer solution in methylene chloride was found to be close to unity over the entire dose-rate range investigated.

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For the monomer solution in diethyl ether, regenerative chain transfer played an important role in determining the molecular weight of the polymer. For the solution in methylene chloride, however, chain transfer appeared to be less important.

INTRODUCTION

The radiation-induced cationic polymerization of isobutyl vinyl ether (IBVE) in bulk under extremely dry conditions has been studied by several investigators [1-4]. An investigation [5, 6] in which the bulk monomer was dried using molecular sieves as the sole drying agent was also carried out by the authors. From a radiation-technological point of view, however, the radiation polymerization of IBVE in solution seems more promising than the bulk polymerization. Apart from the investigation carried out by Stannett and Stahel [7] on the solution polymerization of IBVE in methylene chloride on a small-scale pilot-plant system, no information is available on the kinetics of the solution polymerization of the vinyl ethers by means of gamma radiation.

It was thus decided to investigate the radiation-induced ionic polymerization of IBVE in solution under laboratory conditions where molecular sieves were used as the sole drying agent for the monomer and the solvents. This investigation provided the opportunity to obtain kinetic information for the solution polymerization which could not easily be obtained from the pilot-plant studies. More light is also shed on the high activation energy associated with the propagation reaction, and the apparent change in the activation energy at higher temperatures (ascribed to the solvation of the propagating carbonium ion by the oxygen atoms of the monomer [2, 6]), by using methylene chloride and diethyl ether as solvents. Methylene chloride is well known for the sensitizing effect that it has on radiation-induced ionic polymerizations [8, 9], whereas diethyl ether is closely related in structure to the monomer. The role of regenerative chain-transfer processes in determining the molecular weight of the polymer could also be investigated in detail.

EXPERIMENTAL

Isobutyl vinyl ether was obtained from Eastman Organic Chemicals and was of an industrial grade. The monomer was vacuum-distilled at 25°C on a fractionating column.

Methylene chloride was obtained from Fisher Scientific Co. and was of analytical grade. This solvent was given a single distillation on a

fractionating column and was then used without any further treatment. The mole fraction of the monomer was kept at a constant value of 0.4 in all solutions in methylene chloride.

Diethyl ether was also obtained from Fisher Scientific Co. and was of anhydrous analytical grade. This solvent was given no further treatment and the original container was opened immediately before use. In this solvent the monomer was used at a constant mole fraction of 0.3 in solution.

Davison molecular sieves were used for drying the monomer and the solvents, and were obtained from Fisher Scientific Co. Type 3A (Grade 564), 8-12 mesh sieves with an effective pore size of 3 Å were used.

The irradiations were carried out in the nominal 6 kCi ^{60}Co source of the Department of Chemical Engineering of the North Carolina State University at Raleigh. Irradiations at high dose rates were carried out with the Dynamitron of Columbia Research Corp. at Gaithersburg, Maryland.

The dry solutions were obtained by treating the monomer and solvents separately with molecular sieves, as discussed in detail elsewhere [10].

Viscosity measurements were carried out with benzene as solvent for the polymer at 30°C, using an Ubbelohde capillary viscometer. The weight-average molecular weights were calculated from the intrinsic viscosity by using

$$[\eta] = 7.55 \quad 10^{-5} \overline{M}_w^{0.75}$$

The number-average molecular weights, $\overline{M}_n$, were estimated on the basis of $\overline{M}_w = 2\overline{M}_n$, as confirmed by Ueno [12].

The density of the monomer and the solutions in methylene chloride and diethyl ether at different temperatures was determined experimentally, using a picnometer and a constant temperature bath. In the case of the solutions the densities at temperatures above the boiling points of the solvents were approximated by extrapolation of the experimental data to the higher temperatures.

RESULTS AND DISCUSSION

The Williams Model for Ionic Solution Polymerization

In radiation-induced solution polymerizations the nature of the intermediates and products from the irradiation of the solvent can play an important role, and in some cases severe complications can set in due to a "reactivity transfer" between solvent and monomer, which affects the primary processes which lead to the formation of the transient
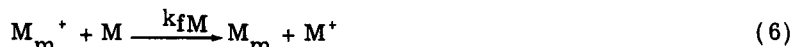
species. The kinetics of radiation-induced solution polymerizations thus often presents formidable problems of interpretation. In discussing the results, no attempt will be made to go into great detail in discussing the kinetics of the system, but the observed effects will preferably be explained in a qualitative way.

On the basis of earlier investigations [6, 4] we can assume that the radiation polymerization of IBVE proceeds by a cationic mechanism. The model of Williams [13] can be modified in the following way to describe the solution polymerization:
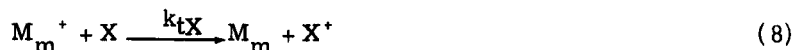
Initiation:

$$\text{Monomer} \xrightarrow{\hspace{1cm}} \cdot M_i^+ + Y^-, \qquad R_{iM} = IG_{iM}/100 \tag{1}$$

$$\cdot M_i^+ + M \xrightarrow{k_{iM}} \cdot M - M^+ \tag{2}$$

$$\text{Solvent} \xrightarrow{\hspace{1cm}} \cdot S_i^+ + Z^-, \qquad R_{iS} = IG_{iS}/100 \tag{3}$$

$$\cdot S_i^+ + M \xrightarrow{k_{iS}} S + \cdot M^+ \tag{4}$$

Propagation and transfer:

$$M_m^+ + M \xrightarrow{k_{pM}} M_m^+ + 1 \tag{5}$$

$$M_m^+ + M \xrightarrow{k_{fM}} M_m + M^+ \tag{6}$$

$$M_m^+ + S \xrightarrow{k_{tS}} M_m + S^+ \tag{7}$$

Termination by impurities:

$$M_m^+ + X \xrightarrow{k_{tX}} M_m + X^+ \tag{8}$$

Termination by recombination:

$$M_m^+ + Y^- \xrightarrow{k_t} \text{polymer} \tag{9}$$

In this scheme, M_m^+ represents the growing cationic polymer chains, X represents impurities that terminate the cationic polymerization process, and $[Y^-]$ and $[Z^-]$ represent the total concentration of all negative species resulting from the monomer and solvent, respectively.

The relative importance of the proton transfer process between monomer and solvent (Reactions 4 and 7) will depend on the relative proton affinities of the monomer and solvent. The proton affinity of diethyl ether has a value of about 200 kcal/mole [14]. Although the proton affinity of IBVE is not available, it is known that the proton affinity increases with an increase in size of the molecule [15] and,

accordingly, we can assume that the proton affinity of the monomer will be well in excess of 200 kcal/mole. In the case of diethyl ether as solvent for IBVE, proton transfer from solvent to monomer is more likely to take place than the reverse process, and Reaction (4) will be more important than Reaction (7). The free ions formed by the radiation of the diethyl ether can, through Reaction (4), act as an additional source of chain-initiating species. As follows from Fig. 1, the rate of polymerization of IBVE is markedly enhanced by the presence of diethyl ether from temperatures above -10°C—in good agreement with the predictions of the model. By invoking steady-state kinetics, the rate of polymerization can, according to the model of Williams [13], be expressed as follows when diethyl ether is used as the solvent:

$$R_p = \frac{R_i(k_{pM}[M]}{(R_i k_t)^{0.5} + k_{tX}[X]} \tag{10}$$

where $R_i = R_{iM} + R_{iS}$, and the assumption is made that the chain-termination reaction by the solvent, Reaction (7), does not play an important role.

The proton affinity of methylene chloride has a value of about 120 kcal/mole [15] and, accordingly, one would expect this solvent to promote the rate of polymerization even better than diethyl ether. It follows from Fig. 1, however, that, for the dry solution of the monomer in methylene chloride, the solvent retards the rate of polymerization over the entire temperature range investigated. This apparent discrepancy can be explained in terms of the terminating effect of the chloride anion, resulting from the radiolysis of the methylene chloride [16], on the propagating carbonium ion:

$$CH_2Cl_2 \xrightarrow{\quad\sim\sim\quad} \overset{+}{CH_2}Cl + Cl^- \tag{3a}$$

$$-M_m^+ + Cl^- \xrightarrow{\quad k_{ts}\quad} -M_m Cl \tag{11}$$

We postulate that the CH_2Cl^+ ion formed in Reaction (3a) is stable enough not to act as a new chain-initiating species, resulting in a decrease in the rate of polymerization. This chain termination by the solvent is similar to Reaction (7). As opposed to the case where diethyl ether is used as solvent, Reaction (7) dominates the promoting effect of Reaction (4), and the rate of polymerization in the presence of methylene chloride can thus be expressed as
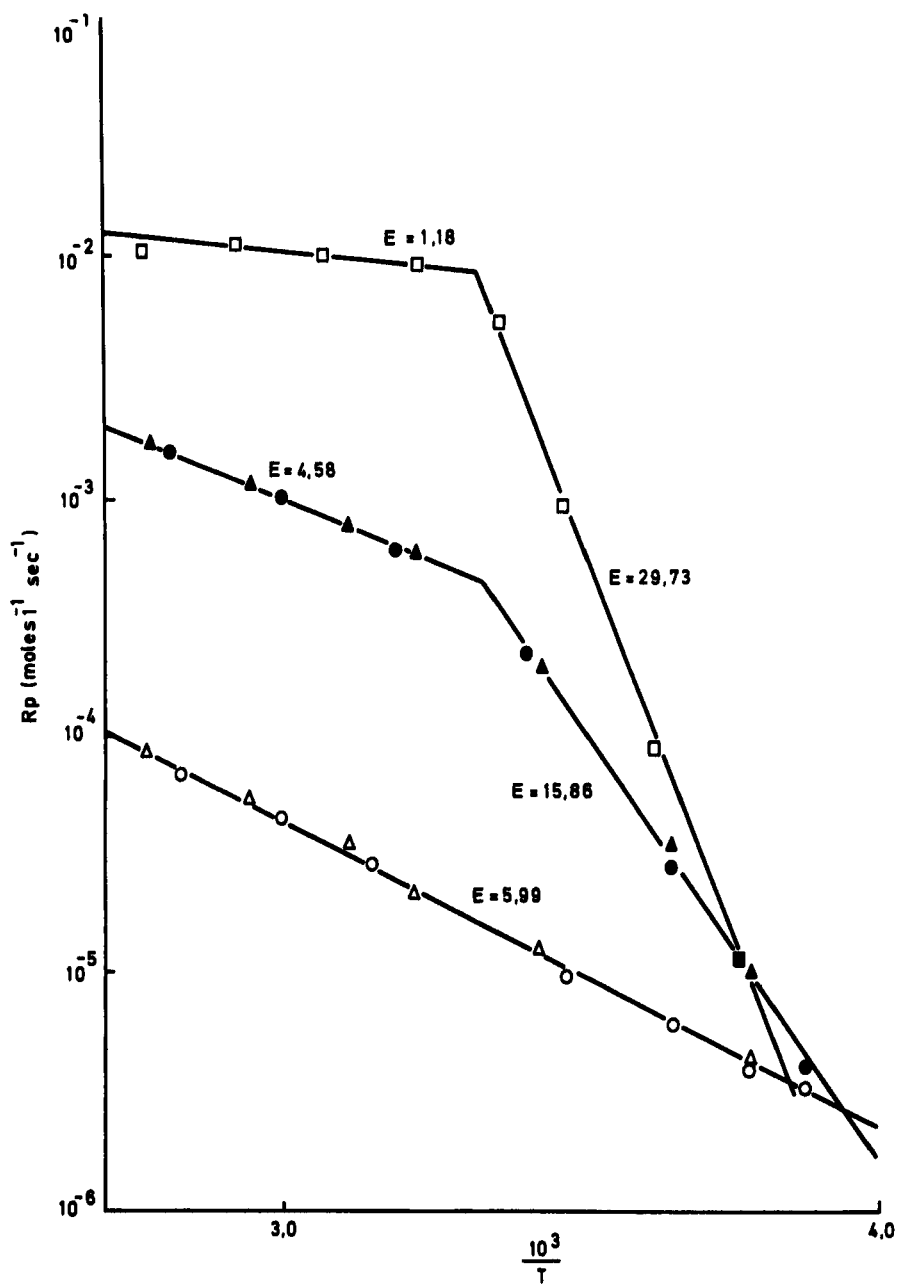
FIG. 1. The rate of polymerization as a function of the irradiation temperature and at a dose rate of 1.2×10^{16} eV/(g)(sec) for ($\square$) IBVE in diethyl ether, ($\blacktriangle$, $\bullet$) IBVE in bulk, and ($\triangle$, $\circ$) IBVE in methylene chloride.

$$R_p = \frac{R_i k_{pM}[M]}{(R_i k_t)^{0.5} + k_{tX}[X] + k_{tS}[S]}$$ (12)

where $R_i = R_{iM}$.

As follows from Fig. 2, the presence of methylene chloride in water-saturated monomer definitely enhances the rate of polymerization. This observation is in good agreement with results reported earlier [8, 9]. For the dried monomer, however, the presence of methylene chloride has a definite retardation on the rates of polymerization over the whole temperature range investigated, as follows from Fig. 1.

The enhancing influence of methylene chloride with a "wet" monomer was ascribed by Szwarc [17] to the decomposition of the water in its dimeric form (this form being a very good scavenger for the ionic polymerization process) to single water molecules which are less efficient as ionic scavengers. The methylene chloride would then lead to an increase in the rate of polymerization, as was found
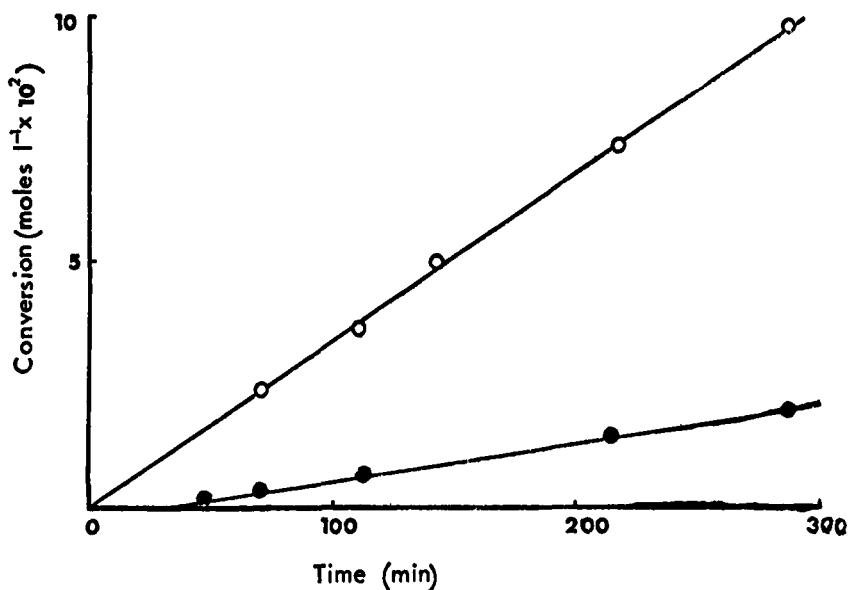
FIG. 2. The conversion as a function of the irradiation time at $0°C$ for water-saturated IBVE at a dose rate of 1.4×10^{16} eV/(g)(sec), in the presence (o) and absence of methylene chloride (•).

experimentally. At the very high levels of dryness, however, the methylene chloride merely terminates the growing carbonium ion through charge neutralization, as indicated in Reaction (11). The investigation has clearly pointed out that methylene chloride only has an advantage as a sensitizing agent in "wet" monomers, but at high levels of dryness it lowers the rate of polymerization.

Dose-Rate Dependence of the Rate of Polymerization

The dose-rate dependence of the rate of polymerization was investigated only in the case of methylene chloride as a solvent for the monomer. At the high concentration of the solvent, as used in the present investigation, the termination reaction by the solvent plays an important role, and $k_{tS}[S] \gg (R_i k_t)^{0.5}$ in Eq. (12). Accordingly, $R_p \propto I$, which is in good agreement with the value of 0.95 found experimentally and indicated in Fig. 3. Although the model predicts a decrease in the dose-rate dependence of R_p with an increase in the dose rate, extension of the dose-rate range by four orders still fails to bring about a diminution from the value of 0.95 shown in Fig. 3. This effect can be ascribed to the high concentration of the solvent, resulting in the termination reaction by the solvent being important even at very high dose rates.

A run was also carried out in which the methylene chloride solution of the monomer was saturated with water. In this case the water can be considered to be an "impurity," and the termination reaction by impurities (Reaction 8) also plays an important role. The dose-rate dependence of R_p in this case has a value of unity—in good agreement with theoretical expectations.

Temperature Dependence of the Rate of Polymerization

As follows from the Arrhenius plots in Fig. 1, there are marked differences in the temperature dependences of the rates of polymerization of the IBVE when diethyl ether and methylene chloride are used as solvents. In the case of methylene chloride as solvent there is no apparent change in the activation energy with an increase in temperature—a phenomenon which is found for the bulk monomer and which is even more pronounced when the monomer is dissolved in diethyl ether as solvent.

In the case of the bulk monomer, the very high activation energy and the change with temperature was ascribed to the solvation of the propagating carbonium ion by the oxygen atoms of the monomer [2, 6].
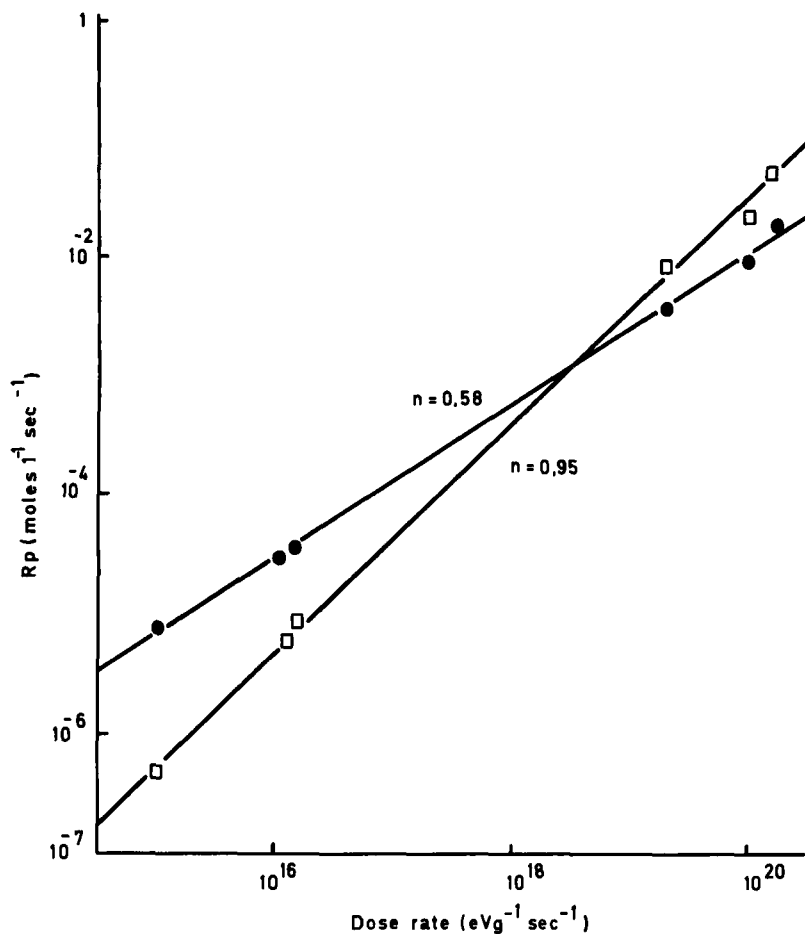
FIG. 3. The dose-rate dependence of the rate of polymerization at 0°C for IBVE in bulk ($\bullet$) and in methylene chloride solution ($\square$). $R_p \propto I^n$.

In order to throw more light on this solvation theory, it was decided to use, as solvent for the monomer, diethyl ether—a molecule which is fairly similar in structure to that of the monomer but less bulky. Using diethyl ether as solvent, one would expect the effect of solvation to be even more pronounced than in the case of the bulk monomer

because of the smaller size of the solvent molecule and hence more efficient in solvating the propagating carbonium ion. As follows from Fig. 1, this is exactly what happens when the monomer is dissolved in diethyl ether: below $30°C$ the apparent activation energy for the diethyl ether solution has a value of 29.7 kcal/mole as opposed to a value of 15.9 kcal/mole found for the bulk monomer. Both activation energies change sharply above $30°C$, the temperature at which it is proposed that the solvation effect is destroyed. The reason why the activation energy drops so low in the case of the solution in diethyl ether is not clear.

In the case of methylene chloride being used as solvent for the monomer, the apparent activation energy has a value of 6.0 kcal/mole over the entire temperature range investigated, as is shown in Fig. 1. It thus appears that this solvent prevents the solvation of the propagating carbonium ion by the monomer molecules over the entire temperature range investigated. This value of the activation energy of 6.0 kcal/mole is very close to the value of 4.6 kcal/mole for the bulk monomer above $30°C$.

These results appear to give further support to the theory of solvation of the propagating carbonium ion proposed by Hayashi [2] and observed by the present authors [6].

The Role of Chain-Transfer Processes

The relative importance of the propagation reaction and the reaction of regenerative chain-transfer to monomer (Reactions 5 and 6, respectively), can be gauged from the absolute magnitude of $G(-m)/\overline{DP}_n$. When this quantity exceeds unity for an ionic process, it is fairly safe to assume that chain transfer is important in determining the molecular weight of the polymer [13]. It follows from Table 1 that, for the solution of monomer in methylene chloride, such processes only become important above $70°C$. For the monomer solution in diethyl ether, however, $\overline{DP}_n$ is governed solely by the transfer constant in Reaction (6).

The difference between the two solvents for the monomer probably results from the difference in molecular structure between methylene chloride and the monomer, on the one hand, and from the similarity in structure between diethyl ether and the monomer, on the other. Charge transfer from the propagating carbonium ion to the solvent is less likely to take place for methylene chloride than for diethyl ether if their relative proton affinities are taken into account [14, 15]. This is also revealed in the marked difference in rates of polymerization in the two solvents, as shown in Fig. 1. It thus appears that in methylene chloride $\overline{M}_n$ is largely determined by charge neutralization through Reaction (11), while in diethyl ether $\overline{M}_n$ is determined solely

TABLE 1. The Effect of Irradiation Temperature on the Chain-
Transfer to Monomer in the Radiation-Induced Polymerization of
IBVE in Bulk and Solution at a dose rate of 1.25×10^{16} eV/(g)(sec)
and a Total Dose at 5.38×10^{19} eV/g

System	Temp ($^\circ$C)	DP_n	$G(-m)$	$G(-m)DP_n$
Bulk	0	760	185	0.24
	10	840	520	0.62
	20	970	1,510	1.56
	30	1,300	3,070	2.36
	40	1,150	3,950	3.44
	50	850	5,120	6.02
	60	650	6,670	10.26
	70	520	8,110	15.60
	80	430	10,300	23.95
	90	380	12,190	32.08
Methylene chloride	10	190	45	0.24
	20	240	60	0.25
	30	300	90	0.30
	40	380	120	0.32
	50	470	160	0.34
	60	460	220	0.48
	70	390	275	0.71
	80	300	360	1.20
	90	220	440	2.00
Diethyl ether	10	90	2,610	29.0
	20	130	16,550	127.3
	30	170	61,090	359.4
	40	190	66,620	350.6
	50	170	69,550	409.0
	60	150	76,840	512.3
	70	120	85,060	708.8
	80	90	89,925	999.2
	90	70	94,940	1,356.3

by charge transfer to monomer and solvent through Reactions (4) and (6).

The relationship between the molecular weight of the polymer formed in the pure monomer and in the solutions can be seen in Fig. 4.
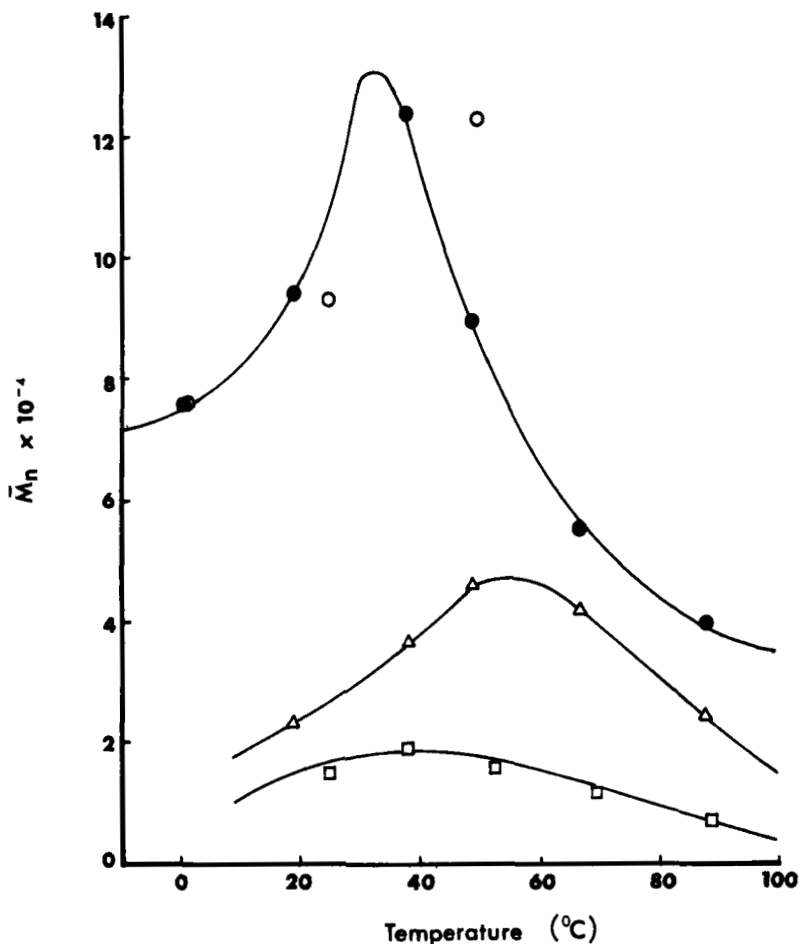
FIG. 4. The number-average molecular weight of poly(IBVE) as a function of the irradiation temperature at a dose rate of 1.25×10^{16} eV/(g)(sec), and a total dose of 5.4×10^{19} eV/g (1 Mrad). ($\bullet$) Bulk monomer, ($\triangle$) methylene chloride solution, ($\square$) diethyl ether solution, and ($\circ$) according to Hayashi [2].

As follows from Fig. 4, the absolute values of $\overline{M}_n$ are much lower in solution than in the bulk phase, and in both solvents $\overline{M}_n$ reaches a maximum value and then decreases with a further increase in temperature.

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