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K. Fujimori^a

^a Department of Physical and Inorganic Chemistry, The University of New England, Armidale, N.S.W., Australia

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Copolymerization of 2,3-Dihydropyran and Ethyl Vinyl Ether with Maleic Anhydride

K. FUJIMORI

Department of Physical and Inorganic Chemistry
The University of New England
Armidale, N.S.W., 2351, Australia

ABSTRACT

2,3-Dihydropyran (DHP) and ethyl vinyl ether (EVE) were copolymerized with maleic anhydride (MA) with benzoyl peroxide at 60°C, and 1:1 alternating copolymers were obtained. The rates were maximum at 1:1 monomer composition. Spontaneous copolymerization and solvent effect on the rate were observed in the copolymerization of DHP with MA, in which initial rates were slower in more polar solvents. Participation of charge transfer complex was considered. EVE copolymerized rapidly with MA, reaching the theoretical limiting conversion of 1:1 alternating copolymerization. Although DHP-MA comonomer pair and EVE-MA comonomer pair formed similar 1:1 charge transfer complexes, DHP copolymerized slowly with MA to produce a low molecular weight copolymer, and the limiting conversion was much lower than the theoretical one. To explain these, degradative chain transfer to DHP monomer is proposed as the initial rate of DHP-MA copolymerization is proportional to the initiator concentration to the power 1.1. Q and e values of DHP were calculated to be 0.013 and -0.93, respectively, from the monomer reactivity ratios of copolymerization of DHP with acrylonitrile [r_1 (DHP) = 0.003 ± 0.006 and r_2 (AN) = 3.6 ± 0.3].

INTRODUCTION

Iwatsuki and Yamashita reported the alternating copolymerization of 2-chloroethyl vinyl ether [1], p-dioxene [1-3], and 1,2-dimethoxyethylene [3] with maleic anhydride (MA) and proposed the participation of the charge transfer (CT) complex into the copolymerization since all the donor-acceptor pairs formed CT complexes. 2,3-Dihydropyran (DHP) and ethyl vinyl ether (EVE) form CT complexes with MA [4, 5]. In this report, copolymerizations of DHP and EVE with MA are studied to see if they form alternating copolymers. DHP is a cyclic ether with allylic hydrogens at the 4 position while EVE is a linear ether without allylic hydrogens. A degradative chain transfer to DHP may be possible in the copolymerization of DHP with MA. Recently chain transfer reactions to N,N-dimethylaniline were reported in alternating copolymerization involving CT complex such as copolymerizations of MA with styrene [6] and the $ZnBr_2$ complex of acrylonitrile with styrene [7].

RESULTS AND DISCUSSION

Stoichiometry of the DHP-MA CT Complex

Intense yellow color develops when DHP and MA are mixed. In chloroform the maximum of the new absorption band attributable to the CT complex was found at $307\text{ m}\mu$, MA being the electron acceptor. The stoichiometry of the complexation was measured as 1:1 by Job's method [8]. The result is shown in Fig. 1. The

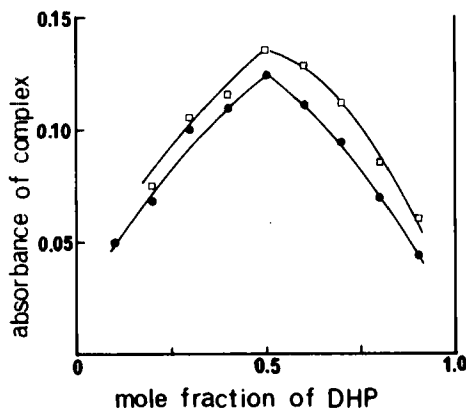


FIG. 1. Ultraviolet determination of stoichiometry of CT complex of DHP with MA in $CHCl_3$ at $21^\circ C$. $[DHP + MA] = 1.40 \times 10^{-2}$ mole/liter (□) At $310\text{ m}\mu$, (●) at $320\text{ m}\mu$.

equilibrium constant of complexation was reported to be 0.11 (liter/mole) in n-heptane at 24°C [4]. EVE forms CT complex with MA with the equilibrium constant of 0.15 (liter/mole) in n-heptane at 24°C [4] and its stoichiometry is 1:1 [5]. That is, the extent of complexation is similar for EVE-MA and DHP-MA comonomer pairs. Kokubo, Iwatsuki, and Yamashita have proposed that the magnitude of the equilibrium constant of CT complexation could be considered as a measure of alternating copolymerizability [1]. But in the case of the DHP-MA comonomer pair, because of the possibility of DHP undergoing degradative chain transfer, the copolymerization behavior is expected to be different from other MA-vinyl ether comonomer pairs of similar equilibrium constants such as the EVE-MA pair.

Q and e Values of DHP

Since no copolymerization data is available for DHP, the copolymerization of DHP with acrylonitrile ($Q = 0.60$, $e = 1.20$ [9]) was carried out using benzoyl peroxide (BPO) at 60°C to calculate Alfrey-Price Q and e values [10] for the characterization of DHP monomer. The results are given in Tables 1 and 2. The monomer reactivity ratios were calculated by the Fineman-Ross method [11] to be r_1 (DHP) = 0.003 ± 0.006 and r_2 (AN) = 3.6 ± 0.3 . From these values and Q and e values of AN, which was used as the standard monomer, values of Q and e of DHP were calculated by

$$r_1 = (Q_1/Q_2) \exp\{-e_1(e_1 - e_2)\}$$

$$r_2 = (Q_1/Q_2) \exp\{-e_2(e_2 - e_1)\}$$

The parameters Q and e were related to the resonance stabilization and polarizability of the monomer, respectively. When compared with Q and e values of linear vinyl ethers, the smaller values of Q and e of DHP may be due to the unfavorable fixed configuration of DHP preventing the π -orbitals of the double bond from entering full conjugation with the oxygen nonbonding orbital and the hyperconjugation with C-H bonds at the 4 position. The e values of DHP, EVE, and divinyl ether (DVE) become negatively larger in this order as their equilibrium constants of CT complexation with MA in n-heptane at 24°C increase in the same order: $K(\text{DHP-MA}) = 0.11$, $K(\text{EVE-MA}) = 0.15$, and $K(\text{DVE-MA}) = 0.18$ (liter/mole) [4].

Polymerizations

Copolymerization was carried out under the same reaction conditions for the DHP-MA comonomer pair and for the EVE-MA comonomer

TABLE 1. Copolymerization of Dihydropyran with Acrylonitrile
 [DHP + AN] = 2.00 moles/liter, [BPO] = 1.20×10^{-3} mole/liter 60°C
 in benzene

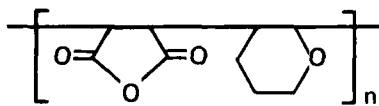
Mole fraction of DHP in feed	Conversion (wt%/min)	N (%)	Mole fraction of DHP in copolymer
0.15	3.69/70	24.47	0.048
0.25	7.20/180	23.36	0.075
0.50	1.02/120	20.06	0.166
0.75	0.98/420	15.06	0.322
0.85	0.67/1170	13.30	0.382

TABLE 2. Alfrey-Price Q and e Values of Vinyl Ethers

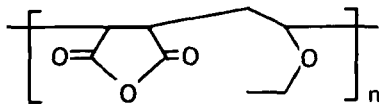
Monomer	Dihydro-pyran	Ethyl vinyl ether [9]	n-Butyl vinyl ether [9]	Divinyl ether [9]	t-Butyl vinyl ether [9]
e	-0.93	-1.17	-1.20	-1.28	-1.58
Q	0.013	0.032	0.087	0.037	0.15

pair. The results are in Tables 3 and 4. Both pairs gave amorphous copolymers which were soluble in polar solvents such as acetone and N,N-dimethylformamide. The IR spectra of polymers showed large absorptions of anhydride group at 1770 and 1850 cm^{-1} and ether linkage at 1080 cm^{-1} . The C=C stretching of DHP at 1645 cm^{-1} and of EVE at 1615 cm^{-1} , and sp^2 C-H stretching of DHP at 3080 cm^{-1} , of EVE at 3160 cm^{-1} , and of MA at 3160 cm^{-1} were completely absent in the polymers, indicating the consumption of C=C double bond by the copolymerization.

MA does homopolymerize but only under drastic conditions [12]. Under the present experimental conditions the homopolymerizations of MA and EVE were almost nil. DHP alone did not give a polymer but a viscous liquid was recovered in 31 wt% after 10 hr under the same condition as the DHP-MA copolymerization. The composition of DHP-MA copolymer was 1:1 over a wide range of monomer composition (Fig. 2). The EVE-MA copolymer also had an almost 1:1 composition despite high conversion. The repeating units of the copolymer were considered as alternating ones:



DHP-MA copolymer



EVE-MA copolymer

TABLE 3. Copolymerization of Dihydropyran with Maleic Anhydride [DHP + MA] = 2.00 moles/liter, [BPO] = 4.00×10^{-2} mole/liter, 60°C in CHCl_3

Mole fraction of DHP in feed	Conversion (wt%/10 hr)	Mole fraction of DHP in copolymer	Relative viscosity ^a
0.20	2.24	0.494	
0.30	6.38	0.504	1.023
0.40	11.04	0.522	1.021
0.50	11.83	0.517	1.017
0.60	10.74	0.511	1.025
0.70	10.19	0.504	1.025
0.80	8.93	0.501	1.018
0.90	7.88	0.540	1.017

^aIn acetone at 30°C, C = 0.50 g/dl.

TABLE 4. Copolymerization of Ethyl Vinyl Ether with Maleic Anhydride [EVE + MA] = 2.00 moles/liter, [BPO] = 4.00×10^{-2} mole/liter, 60°C in CHCl_3

Mole fraction of EVE in feed	Conversion (wt%/100 min)	Mole fraction of EVE in copolymer	Relative viscosity ^a
0.20	14.20	0.455	1.107
0.35	46.74	0.462	1.231
0.50	83.41	0.494	1.306
0.65	64.67	0.514	1.418
0.80	38.62	0.497	1.320

^aIn acetone at 30°C, C = 0.50 g/dl.

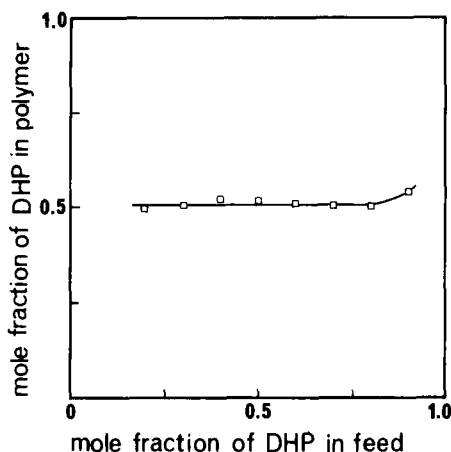


FIG. 2. Copolymer composition curve for the copolymerization of DHP with MA at 60°C in CHCl_3 .

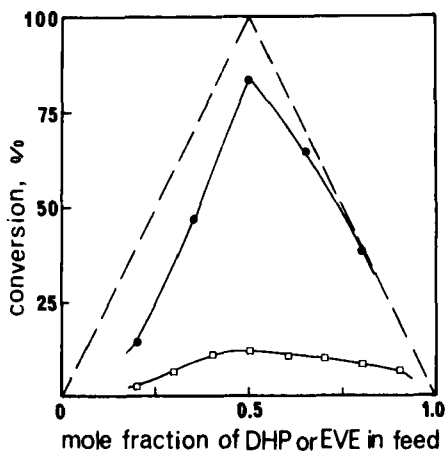


FIG. 3. Conversion of copolymerization of DHP with MA after 10 hr (\square) and conversion of copolymerization of EVE with MA after 100 min (\bullet). The dotted lines show the maximum yields possible for pure alternating copolymers. $[\text{Donor} + \text{MA}] = 2.0$ mole/liter, $[\text{BPO}] = 4.0 \times 10^{-2}$ mole/liter, at 60°C in CHCl_3 .

The conversion of the copolymerization of DHP with MA after 10 hr is compared with that of the copolymerization of EVE with MA after 100 min in Fig. 3. The copolymerization of DHP with MA proceeded

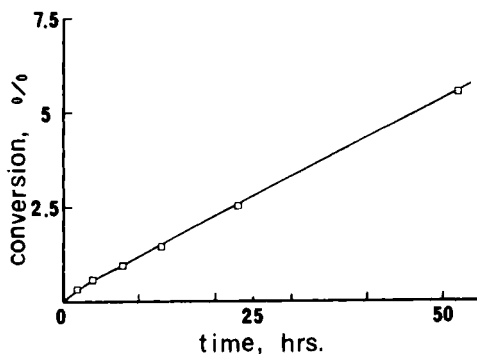


FIG. 4. Time-conversion curve of spontaneous copolymerization of equimolar amounts of DHP and MA in bulk at 60°C.

very slowly, showing a broad maximum rate at 1:1 monomer composition. When prolonged polymerization was carried out starting with a 1:1 monomer ratio, the limiting conversion was only 25 wt% after 72 hr. On the other hand, EVE copolymerized rapidly with MA, approaching the theoretically maximum conversion of 1:1 alternating copolymerization within 100 min. This, together with the 1:1 alternating structure of the EVE-MA copolymer, is consistent with the previously reported results of other vinyl ethers with MA by Kokubo, Iwatsuki, and Yamashita, for which participation of the CT complexes in the copolymerizations has been proposed. But in the case of DHP-MA comonomer pair, the participation of the CT complex and degradative chain transfer to DHP are considered in addition to the fact that DHP is a 1,2-disubstituted ethylene, which is generally regarded much less reactive than monosubstituted ethylenes.

Spontaneous copolymerization occurred as soon as DHP and MA were mixed at room temperature, probably being initiated by the CT complex. The time-conversion curve of bulk spontaneous copolymerization of the DHP-MA system at 60°C is shown in Fig. 4.

It has been shown [1, 4] that the equilibrium constant of CT complexation decreases with the increase of solvent polarity, since in polar solvents free monomers are better stabilized than the complex of the monomers. Specific modes of each solvent to solvate monomers must not be neglected. Nevertheless, a general decrease of the rate of DHP-MA copolymerization was observed with increasing dielectric constant of the solvents measured at 25°C [13] (Fig. 5), which was consistent with the CT complex participation. In a more polar solvent the amount of complex formed would be less, hence the rate of polymerization would be smaller. Thus participation of the 1:1 CT complex formed by the comonomers could be an explanation for the 1:1 alternating copolymer and the rate maximum at the 1:1 monomer composition.

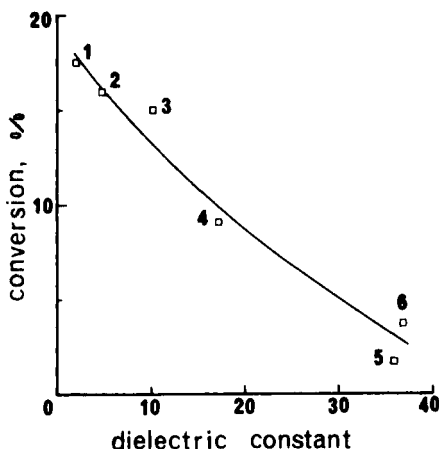
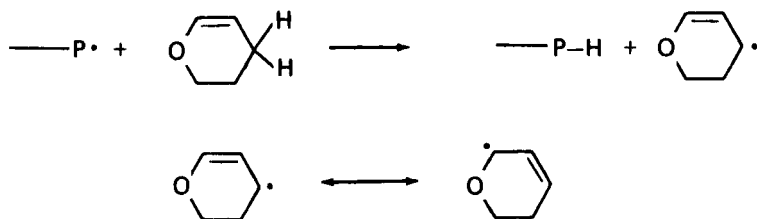


FIG. 5. Effect of the polarity of solvents on the conversion of equimolar copolymerization of DHP with MA after 10 hr at 60°C. $[\text{DHP} + \text{MA}] = 1.86$ mole/liter, $[\text{BPO}] = 1.82 \times 10^{-2}$ mole/liter. (1) Dioxane, (2) chloroform, (3) 1,2-dichloroethane, (4) acetophenone, (5) nitromethane, and (6) dimethylformamide.

If the termination reactions of the copolymerization are biradical, the initial rate of the copolymerization should be proportional to the square root of the initiator concentration, and if the termination is a degradative chain transfer, the rate of the copolymerization will be proportional to the first power of initiator concentration [14]. The initial rate of copolymerization of the DHP-MA comonomer pair measured at 1:1 monomer composition is plotted against the initiator concentration on a log-log scale in Fig. 6. The slope of the straight line is close to unity, i.e., $R_p \propto [I]^{1.1}$, which suggests that the slow rate of copolymerization and the low molecular weight of the DHP-MA copolymer may be due to the degradative chain transfer to DHP, the allylic hydrogen at the 4 position being responsible for it. The resulting allylic radical would be so stabilized by resonance that it could not reinitiate polymerization effectively:



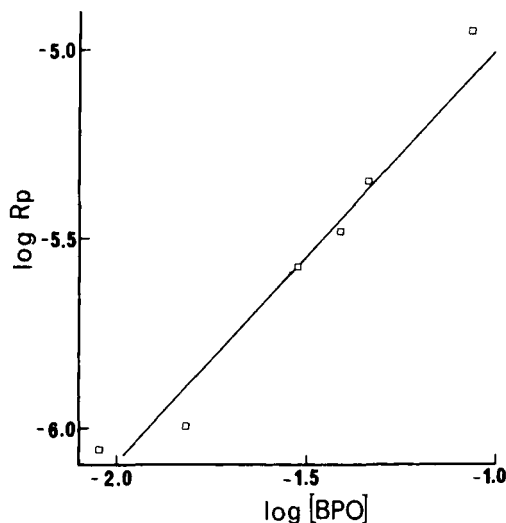


FIG. 6. Dependence of rate of copolymerization of DHP with MA, R_p (mole/liter-sec), on initiator concentration, $[BPO]$ (mole/liter). $[DHP + MA] = 6.11$ mole/liter, $[DHP]/[MA] = 1$, at $60^\circ C$ in benzene.

EXPERIMENTAL

Commercially available reagent grade chemicals were distilled (DHP, EVE, AN, and solvents) or recrystallized (MA from benzene, and BPO from methanol) before use.

Polymerizations were carried out in glass tubes of 10 to 40 ml capacity sealed under high vacuum after freeze-thaw degassing. The tube was then immersed in an oil thermostat. The DHP-AN copolymer was isolated by reprecipitations in benzene from acetone solution. The DHP-MA and the EVE-MA copolymers were purified by reprecipitating acetone solutions into dry diethyl ether.

A UNICAM SP800 UV spectrophotometer and a UNICAM SP200 IR spectrophotometer were used.

The composition of DHP-MA and EVE-MA copolymers was measured by high-frequency conductometric titration with a Philips PR9500 bridge. The copolymers were dissolved in aqueous NaOH solution and back-titrated with HCl solution. The composition of the DHP-AN copolymer was calculated from the nitrogen content measured by the Australian Microanalytical Service.

Viscosity was measured with an Ostwald-Fenske viscometer in acetone solution at $30^\circ C$.

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