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Radical Copolymerization of 2-Methyl-2-vinyl-1,3-dioxolane with Acrylonitrile

Natsuki Yamashita[a]; Yasuo Mori[a]; Masakuni Yoshihara[a]; Toshihisa Maeshima[a]
[a] Department of Applied Chemistry Faculty of Science and Engineering, Kinki University, Higashi, Osaka, Japan

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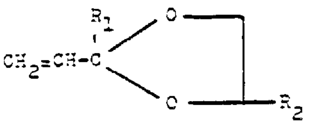
LETTER TO THE EDITOR

Radical Copolymerization of 2-Methyl-2-vinyl-1,3-dioxolane with Acrylonitrile

NATSUKI YAMASHITA, YASUO MORI, MASAKUNI YOSHIHARA, and TOSHIHISA MAESHIMA

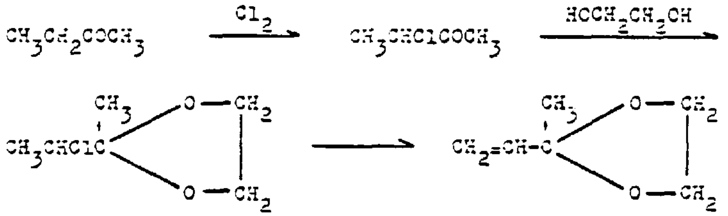
Department of Applied Chemistry
Faculty of Science and Engineering
Kinki University
Higashi-Osaka, Japan

It has been reported that allylic monomer has low polymerizability because of degradative chain transfer [1-3]. In previous papers [2, 3] we have shown that the polymerizability of vinyl acetal might be based upon the ability of hydrogen abstraction at the allylic proton by the propagating radical. In order to investigate this effect further, 2-methyl-2-vinyl-1,3-dioxolane (I) was synthesized and copolymerized with acrylonitrile (AN) in dimethylformamide (DMF) at 60° C. The results will be compared with those of 2-vinyl-1,3-dioxolane derivatives.



I : $R_1=CH_3$, $R_2=H$
II : $R_1=R_2=H$
III : $R_1=H$, $R_2=CH_3$
IV : $R_1=H$, $R_2=CH_2OH$

Monomer I was prepared from methyl ethyl ketone as follows:



(I)

Chlorination was carried out by the method described by Rabjohn et al. [4] (yield, 18%). Acetalic condensation was carried out according to Fischer's method [5] (yield, 54%; bp, 66-67°C/11 Torr). Dehydrochlorination was carried out as follows: 500 g of diethylene glycol, about 250 g of potassiumhydroxide, and 50 g of chlorinated acetal were placed into a 1-liter flask equipped with an agitator, condenser, and N_2 line. The solution was heated at 95°C for 5 hr and then distilled from the reaction mixture. The product obtained, I, was characterized by elemental analysis and IR and NMR spectra (yield, 50%: bp, 112-114°C/706 Torr) [6].

Polymerization was done as described in our previous papers.

The results of the copolymerization of AN (M_1) with I (M_2) are given in Table 1. The increase of the acetal concentration in the monomer feed decreased both the copolymerization rate (R_p) and the number-average molecular weight ($\overline{M}_n$). Such phenomena were observed in the copolymerization of AN with vinyl acetal, which might be affected by the degradative chain transfer of the allyl group [2, 3]. It would not be expected, however, that this mechanism would operate on the polymerizability of I because of the non-existence of an active proton in I. In fact, the chain transfer constant (C_{tr}) of I toward polystyryl radical was determined as about zero (Table 2).

Table 2 also contains the copolymerization parameters as well as the results of other vinyl acetals [2]. All acetals were found to have only weak copolymerizability with AN. It is particularly interesting to note that the monomer reactivity ratio of I was much higher than those of other monomers, in spite of an absence of the degradative chain transfer reaction. One possible explanation is that vinyl group in I might be sterically hindered by both methyl and dioxolane groups, as in the case of polymerizations of α-substituted vinyl monomers [7-9].

TABLE 1. Copolymerizations of AN with I[a]

Charged composition acetal (mole %)	Polymerization time (min)	Conversion (%)	Copolymerization rate (mole/liter sec × 10^{-5})	Incorporated ratio acetal (mole %)	$\bar{M}_n$[b]
10	120	11.22	4.11	2.75	6968
25	190	10.16	2.83	5.64	4918
40	345	10.64	1.82	5.73	4405
55	561	8.30	0.89	12.00	3105
70	1088	5.68	0.34	13.80	2854
85	2810	2.07	0.05	23.69	2135

[a] Polymerization conditions: total volume, 25 ml; total monomers, 0.06 mole; concentration of AIBN, 7.72 × 10^{-3} mole/liter.

[b] VPO method (in DMF at 75°C).

TABLE 2. Chain Transfer Constants (C_{tr}) and Copolymerization Parameters

Monomer	$C_{tr} \times 10^{-4}$	r_1	r_2	Q	e
I	0	11.97	0.01	0.012	-0.25
II[a]	16.60	4.80	0.15	0.020	-0.10
III[a]	14.37	5.85	0.01	0.014	-0.49
IV[a]	2.40	4.25	0.05	0.032	-0.04

[a] Data of previous paper [2, 3].

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