

SPONTANEOUS COPOLYMERIZATION OF 4-METHYLENE-1, 3-DIOXOLANE DERIVATIVES WITH ACRYLONITRILE AND SUBSTITUENT EFFECT

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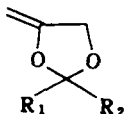
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ABSTRACT

The copolymerization of six 2-substituted 4-methylene-1, 3-dioxolane with acrylonitrile(AN) gives rise spontaneously to the alternating copolymers by the participation of charge-transfer(CT) complexes. The structures of copolymers was ascertained by their IR, ^1H and ^{13}C NMR spectra, etc.. The electron effect of substituents on 2-position of monomer **2** is the most important factor in predicting the reactivity of CT complexes. However the steric effect determines the ring-opening degree of monomer **2**. The spontaneous copolymerization mechanism has been discussed.

INTRODUCTION

Although 2-alkyl substituted 4-methylene-1, 3-dioxolane monomers were indifferent to free radical initiators^[1], the electron-donate monomers **1a** and **1b** spontaneously copolymerized with electron-accept monomers, such as maleic anhydride through the formation of charge-transfer(CT) complexes to yield alternative copolymer^[2,3]. It was found that the alternating tendency between electron donor(D) and electron acceptor(A) monomer was affected by the interaction between them, and the strong interaction favored the formation of alternative copolymer and also the higher yield of copolymer was obtained^[2]. For studying the effect of 2-substituents on the formation of complexes, six monomers(**2a-2f**) were synthesized, their spontaneous copolymerization with acrylonitrile, the composition of copolymers, the steric and electron effect of alkyl substituents on copolymerization activity were studied. The polymerization mechanism was discussed.



1a. $\text{R}_1 = \text{R}_2 = \text{H}$

1b. $\text{R}_1 = \text{R}_2 = \text{CH}_3$

EXPERIMENTAL

1. Synthesis of 2-alkyl-4-methylene-1, 3-dioxolane

The monomers **2** were synthesized according to the reported procedures^[4]. The yields, the boiling points and the ^1H -NMR data of the chlorides and the monomers are listed in Table 1 and 2 respectively.

Table 1 Properties and ^1H NMR data of 2-alkyl-4-chloromethyl-1, 3-dioxolane

Monomer	yield(%)	b.p.	^1H NMR (δ ,ppm)
4-chloromethyl-2-methyl-1,3-dioxolane	71	40°C(10mmHg)	4.9(1H, $-\text{CH}-\text{O}-$); 3.1-4.3(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.25(3H, $-\text{CH}_3$)
4-chloromethyl-2, 2'-dimethyl-1,3-dioxolane	76	55°C(10mmHg)	3.2-4.4(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.3 (6H, 2- CH_3)
4-chloromethyl-2-ethyl-2'-methyl-1, 3-dioxolane	75	65°C(7mmHg)	3.2-4.4(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.6(2H, $-\text{CH}_2-$); 1.3 (3H, $\text{CH}_3-\text{C}-\text{O}-$); 0.9(3H, CH_3)
4-chloromethyl-2-methyl-2'-isopropyl-1, 3-dioxolane	75	74°C(8mmHg)	3.2-4.4(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.7(1H, $-\text{CH}-$); 1.2 (3H, $\text{CH}_3-\text{C}-\text{O}-$); 0.9(6H, 2 CH_3-)
4-chloromethyl-2-methyl-2'-tert-butyl-1, 3-dioxolane	70	63°C(2mmHg)	3.2-4.4(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.2(3H, $\text{CH}_3-\text{C}-\text{O}-$); 0.9(9H, 3 CH_3)
4-chloromethyl-2-cyclohexylidene-1, 3-dioxolane	83	70°C(0.04mmHg)	3.2-4.3(5H, $-\text{CH}_2\text{Cl}$, $-\text{OCH}_2-$, $-\text{CH}-$); 1.5(10H, $\text{CH}_2(\text{CH}_2)_4\text{C}<$)

2. Spontaneous copolymerization

Monomer 2 and acrylonitrile were placed in a two-neck flask, stood at 15°C for 24hrs. The reaction mixture dissolved in CH_2Cl_2 was poured into *n*-heptane while stirring. A white solid copolymer was obtained, and dried at 40°C in vacuum oven for 24hrs.

RESULTS AND DISCUSSION

1. Spontaneous copolymerization

Spontaneous copolymerization of monomer 2d with acrylonitrile was performed at room

Table 2 Properties and ^1H NMR data of 2-alkyl-4-methylene-1, 3-dioxolane

Monomer	yield(%)	b.p.	^1H NMR (δ ,ppm)
4-methylene-2-methyl-1, 3-dioxolane (2a)	55	45°C(90mmHg)	4.1, 3.7(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.3(2H, $-\text{CH}_2\text{O}-$); 1.4(3H, CH_3-); 5.2(1H, $\text{HC} \begin{smallmatrix} \text{O}- \\ \diagdown \end{smallmatrix} \diagup \text{O}-$)
4-methylene-2,2'-dimethyl-1, 3-dioxolane (2b)	60	110°C(760mmHg)	4.1, 3.7(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.3(2H, $-\text{CH}_2\text{O}-$); 1.4(6H, 2CH_3)
4-methylene-2-ethyl-2'-methyl-1, 3-dioxolane (2c)	86	72°C(102mmHg)	4.1, 3.6(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.3(2H, $-\text{CH}_2\text{O}-$); 1.7(2H, $-\text{CH}_2-$); 1.3(3H, $\text{CH}_3-\text{C} \begin{smallmatrix} \text{O}- \\ \diagdown \end{smallmatrix} \diagup \text{O}-$); 0.9(3H, CH_3)
4-methylene-2-isopropyl-2'-methyl-1, 3-dioxolane (2d)	60	64°C(57mmHg)	4.1, 3.6(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.3(2H, $-\text{CH}_2\text{O}-$); 1.9(1H, $-\text{CH}-$); 1.2(3H, $\text{CH}_3\text{C} \begin{smallmatrix} \text{O}- \\ \diagdown \end{smallmatrix} \diagup \text{O}-$); 0.9(6H, 2CH_3)
4-methylene-2-t-butyl-2'-methyl-1, 3-dioxolane (2e)	70	42°C(1mmHg)	4.1, 3.7(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.4(2H, $-\text{CH}_2\text{O}-$); 1.3(3H, $\text{CH}_3\text{C} \begin{smallmatrix} \text{O}- \\ \diagdown \end{smallmatrix} \diagup \text{O}-$); 0.8(9H, 3CH_3)
4-methylene-2-hexylidene-1, 3-dioxolane (2f)	70	44°C(0.04mmHg)	3.7, 4.1(2H, $\text{H}_2\text{C} = \text{C} \leq$); 4.3(2H, $-\text{CH}_2\text{O}-$); 1.6(10H, $\text{CH}_2(\text{CH}_2)_4\text{C} \leq$);

Table 3 Spontaneous copolymerization of 4-methylene-2-isopropyl-2'-methyl-1, 3-dioxolane(2d) with acrylonitrile

Copolymerization conditions ^{a)}			Copolymer		Extent of	$\overline{M}_n$ ^{d)}	$\frac{\overline{M}_w}{\overline{M}_n}$ ^{d)}
Initiator	Solvent	atmosphere	yield	acceptor ^{b)}	Ring-opening of monomer 2		
(mole%)	(ml)		(%)	(%)	(%) ^{c)}		
—	chlorobenzene						
	(5ml)	N ₂	4	51	26	1520	2.0
—	chlorobenzene						
	(5ml)	air	13	55	23	1130	1.8
AIBN(0.5)	chlorobenzene						
	(5ml)	N ₂	24	53	2	3340	2.2
—	bulk	air	45	51	18	1770	2.9

a. monomer 2d, 0.01mole; AN, 0.01mole; 55°C; 24h,

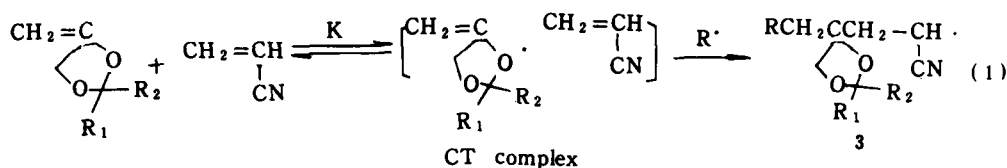
b. calculated from N% of element analysis

c. calculated from the data of ^1H NMR spectra.

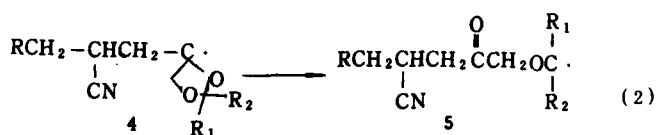
d. determined by GPC on Waters Model 150C instrument using polystyrene standards in THF at 25°C.

temperature in nitrogen or air atmosphere. After purification, a white solid copolymer was obtained. The results are listed in Table 3.

Comparing with the spontaneous copolymerization, the addition of 2, 2'-azobisisobutyronitrile(AIBN) into the copolymerization system enhances the yields of the copolymers and decreases the content of ring-opening units in copolymers (see Table 3). The fact indicated that the primary radical attacks the double bond attached to 1,3-dioxolane in CT complex



to yield radical **3** which is stabilized by CN group (reaction 1), that is, the less attack of chain radical to acrylonitrile takes place to form radical **4** which undergoes ring-opening polymerization (reaction 2).



2. Structure of copolymer

When copolymerization of monomer **2c** and AN was carried out in a two-neck flask at room temperature without initiator, a white copolymer was obtained after purification. The appearance of the absorption bands at 2200cm^{-1} ($-\text{CN}$) and $1140, 1060\text{cm}^{-1}$ ($-\text{C}-\text{O}-$) on IR spectra of copolymer **2c**-AN (see Fig.1c) demonstrates the occurrence of copolymerization of **2c** with AN. An absorption band at 1720cm^{-1} on the IR spectrum (Fig.1c) and a signal at 207ppm on the ^{13}C NMR spectrum (Table 4) corresponding to the ketone carbonyl group are the result of ring-opening polymerization of monomer **2c**. The peak at 3.3—4.2ppm (see Fig.2) corresponding to methylene protons attached to an oxygen and the signal at 112.7ppm (Table 4) corresponding to ketal carbon indicate that monomer **2c** undergoes addition polymerization. Based on the above discussion, the structure of the copolymer can be determined (see structure **6**) and the carbon chemical shifts of copolymer **6** are listed in Table 4.

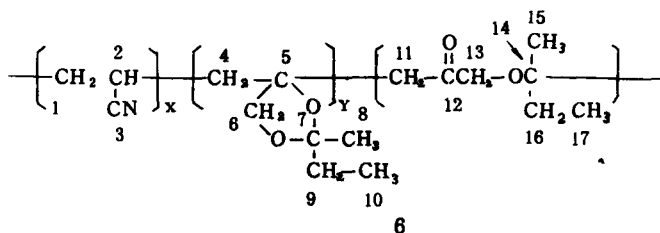


Table 4 ^{13}C NMR(CDCl_3) data of copolymer obtained from monomer **2c** and AN

Carbon	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
$\delta(\text{ppm})$	38.9	28.8	118.1	32.6	79.2	72.5	112.7	22.6	30.9	8.7
Carbon	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇			
$\delta(\text{ppm})$	31.9	207.1	71.7	65.9	14.1	29.0	7.8			

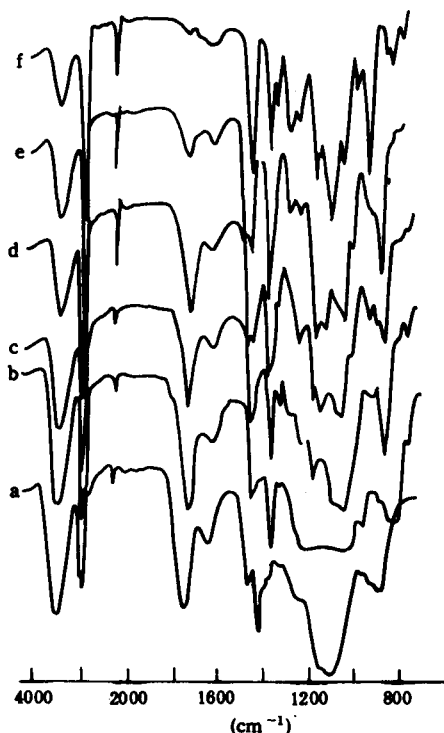


Fig. 1 IR spectra of spontaneous copolymers 2-AN.

a) 2a; b) 2b; c) 2c; d) 2d; e) 2e; f) 2f;

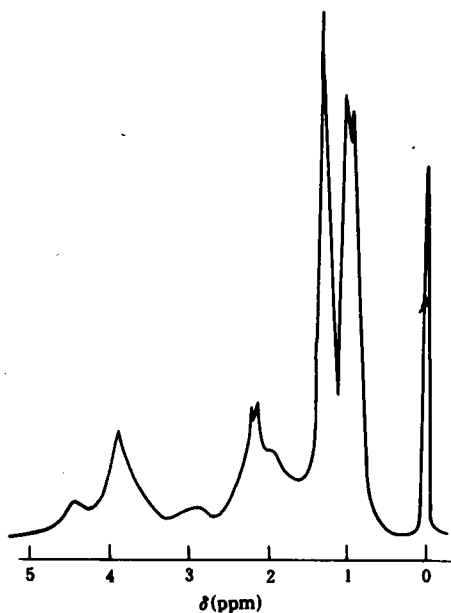


Fig. 2 ^1H NMR spectrum of spontaneous copolymers 2c-AN(CDCl_3)

When various monomer **2** spontaneously copolymerized with AN, similar structures were observed, but the IR spectra of the copolymers show the great content difference of structural units' among them (Fig.1). The gradual decrease of carbonyl absorption strength at 1720cm^{-1} from **2a** to **2f** implies the decrease of ring-opening units in the copolymers. The higher nitrile absorption strength at 2200cm^{-1} of **2d-AN**, **2e-AN** and **2f-AN** than that of **2a-AN**, **2b-AN** and **2c-AN** demonstrates that the former three copolymers contain more acrylonitrile unit. The relative values of the three structural units——addition units of AN and monomer **2**, ring-opened unit of monomer **2**, can be calculated based on the N% from the elemental analysis of copolymers, the integration of the ^1H NMR signals at 3.3—4.2(— CH_2O —), 4.2—5.0ppm(— $\overset{\text{O}}{\text{C}}\text{CH}_2\text{O}$ —) (Fig.2). The results are listed in Tables 3 and 5.

3. The Effects of substituents on spontaneous copolymerization

The results of spontaneous copolymerization of monomer **2** and AN are listed in Table 5. Obviously, the yields and the molecular weights decrease in the following order:

$$2f > 2e > 2d > 2c > 2b > 2a$$

However, the ring-opening degrees of monomer **2** have the opposite order:

$$2a > 2b > 2c > 2d > 2e > 2f$$

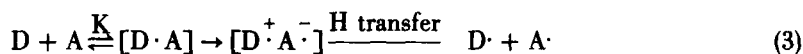
Two factors, steric and electronic effects should be considered for the polymerization reactivity of monomer. Steric and electron effects increase from **2a** to **2e**, since the substituents on 2-position of

Table 5 Spontaneous copolymerization of monomer **2** with AN in air atmosphere^{a)}

Monomer	Copolymer			$\overline{M}_n$ ^{d)}	$\overline{M}_w/\overline{M}_n$ ^{d)}
	yield(%)	AN(mole%) ^{b)}	ring-opening degree ^{c)}		
2a	3.1	33	34	740	1.9
2b	11.7	30	25	840	1.7
2c	16.9	40	24	1290	1.6
2d	36.0	48	18	1890	2.7
2e	37.0	49	5	3910	2.4
2f	58.0	47	6	11780	4.5

a,b,c,d; the same as the footnotes of Table 3.

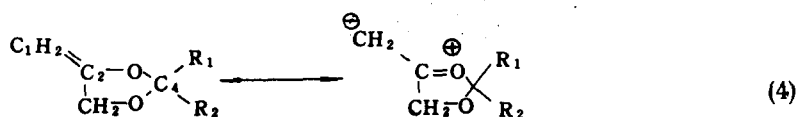
monomer **2** are H, CH₃, CH₂CH₃, CH(CH₃)₂ and C(CH₃)₃. It is obvious that electronic effect is the most important in the spontaneous copolymerization. If there is a greater interaction between the electron donor and acceptor in the CT complex, the radical would be generated by a proton transfer of the dative structure^[5], then copolymerization takes place (reaction 3).



CT complex dative structure

The initiation may be facilitated by the presence of oxygen because oxygen can accept one electron from the acceptor radical anion due to its high electron affinity; this reaction accelerates the generation of the donor radical cation. Thus the yield of spontaneous copolymers in the air is higher than that in the N₂ atmosphere. (see Table 3)

Spontaneous copolymerization reactivity is determined by the concentration of the intermediate $[D^+ \cdot A^-]$ which is related to the interaction between the donor and acceptor. The high degree of p- π conjugation in the vinyloxy group (see reaction 4) might be described by thermal^[4] and NMR data^[6].



By analyzing the obtained ¹³C NMR spectra of monomer **2**, we can find that the relation between chemical shifts (δ) of C₁, C₂, C₄ and the Taft's polar substituent constants (σ_R) for R₁ and R₂ appears linear (see Fig. 3) and a least-squares treatment of $\delta(\text{C}_1, \text{C}_2, \text{C}_4)$ against σ_R ^[7] gives the following equations with a good correlation coefficients (r).

$$\delta(\text{C}_1)/\text{ppm} = 77.64 + 2.87\sigma_R \quad r = 0.992 \quad (5)$$

$$\delta(\text{C}_2)/\text{ppm} = 156.19 - 2.13\sigma_R \quad r = 0.954 \quad (6)$$

$$\delta(\text{C}_4)/\text{ppm} = 112.38 - 16.81\sigma_R \quad r = 0.998 \quad (7)$$

The comparison of three lines on Fig.3 indicates that the substituents R₁ and R₂ have a greater effect on $\delta(\text{C}_4)$ with a large slope (16.81), and also affect the electron density of double bond through

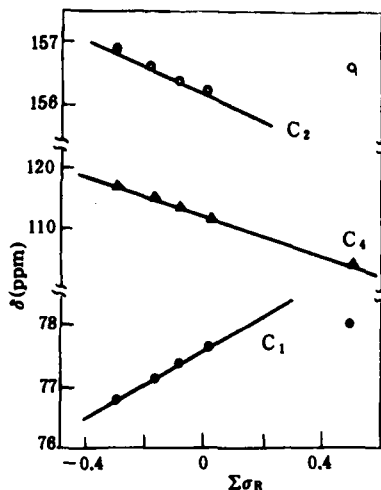
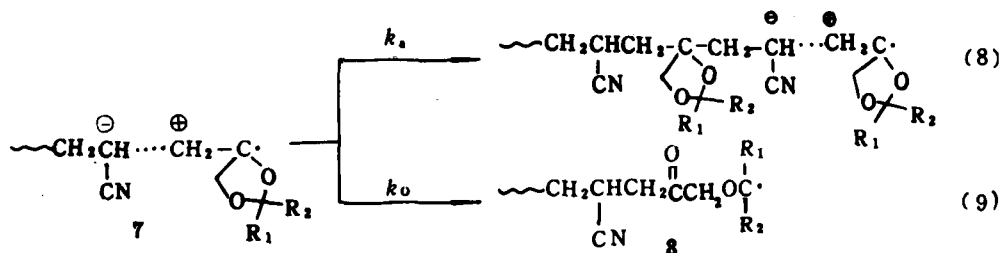


Fig. 3 The value of $\delta(C_1)$ (●), $\delta(C_2)$ (○) and $\delta(C_4)$ (▲) of 2-substituted 4-methylene-1, 3-dioxolanes as a function of $\Sigma\sigma_R$

the p- π conjugation. The presence of a slight excess of negative charge on C_1 has been verified by MO calculations^[8] and experimental evidence^[9]. Thus the ^{13}C chemical shifts of C_1 increase as its negative charge increases, which is the result of the increase of electron-donating effect of substituents. The opposite phenomenon of C_2 was observed. So the polarity of double bond increases in the order of H, CH_3 , CH_2CH_3 , $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$. The greater the polarity of double bond, the stronger the formation of CT complex and the easier the electron transfer from donor to acceptor. Therefore, the yields and molecular weights of copolymers increase in the same order with the polarity of double bond. However the opposite order of ring-opened unit contents in the copolymers was obtained.

Radical 7 may propagate via addition polymerization (reaction 8), or undergo ring-opening reaction to form radical 8 (reaction 9).



The bulky substituent R_1 or R_2 would decrease the rate of addition polymerization of radical 8 with AN because of the steric effect. The polymerization conditions, such as temperature, concentration etc., might affect the ring-opening degree of monomer 2. For example, solution copolymerization favors the intramolecular ring-opening reaction (see Table 3).

From the above discussion, it can be assumed that the reactivity of 2-substituted 4-methylene-1, 3-dioxolane in the CT complex is mainly determined by electronic effect. Tafts' polar constants and ^{13}C NMR shifts of C_1 , C_2 in the double bond can be used to predict the reactivity of CT complex monomer. Steric effect is the most important factor in predicting the tendency of ring-opening polymerization of monomer 2.

Keywords:

Spontaneous copolymerization; 4-methylene-1, 3-dioxolanes; CT complex; Substituent effect

REFERENCE

- [1] Goodman, M. and Abe, A., *J. Polym. Sci. part A*, **1964** **2**, 347.
- [2] Pan C.Y.; Wu Z.; Zhu Q.R. and Bailey, W.J., *J. Macromol. Sci. -Chem.* **1987** **25**(1), 27.
- [3] Fukuda, H.; Hirota, M. and Nakashima, Y.; *J. Polym. Sci. Polym. Chem. Ed.*, **1982** **20**, 1401.
- [4] Dolliver, M.A.; Gresham, T. L.; Kistiakowsky, G.B.; Smith, F.A. and Vaughan, W.E.; *J. Am. Chem. Soc.*, **1930** **60**, 440.
- [5] Fukuda, H.; Hirota, M.; Endo, T.; Okawara, M. and Bailey, W.J.; *J. Polym. Sci., Polym. Chem. Ed.*, **1982** **20**, 2935.
- [6] Taskinen, E.; *J. Org. Chem.*, **1978** **43**(14), 2773.
- [7] Davis, M.A., *J. Org. Chem.*, **1967** **32**, 1161.
- [8] Trofirnov, B.A.; Shergina, N.I.; Kositsyna, E.I.; Atavin, A.S.; Gusarov, A.G.; Gavrilova, G.M. and Yemelynov, I.S.; *Org. React. (USSR)*, **1969** **6**, 902.
- [9] Taskine, E., *Tetrahedron* **1978** **34**, 429.