1978 *Macromolecules* 1994, *27*, 1978–1980

Controlled Zwitterionic Copolymerization of Cyclic Ketene Acetal with Methyl α-Cyanoacrylate in the Presence of Quaternary Ammonium Salts

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Received November 23, 1993
Revised Manuscript Received January 31, 1994

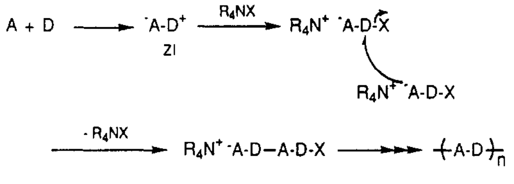
Spontaneous polymerizations of many different pairs of electron donor and acceptor monomers via zwitterion have been reported.[1-3] When one or both of the monomers in the pair are heterocyclic monomers, a stable zwitterion is generated, followed by zwitterion polycombination to afford an alternating copolymer.[1] When they are olefinic monomers, an unstable zwitterion is formed, followed by a zwitterion-initiated ionic chain reaction to afford homopolymers of donor and/or acceptor olefins.[2,3] In the zwitterionic polymerization of a cyclic ketene acetal with acceptor olefins, however, random copolymers have been reported to be obtained exceptionally.[4]

The copolymers in almost all these systems are low in molecular weight except a few examples.[5-7] Recently, Odian et al. reinvestigated the zwitterionic polymerization of 2-methyl-2-oxazoline with acrylic acid and have reported the mechanism responsible for the low molecular weight.[8] Hence, high molecular weight polymers can be obtained in the zwitterionic polymerization by using isolable zwitterions[9,10] or a molecule containing both nucleophilic and electrophilic groups affording zwitterion upon heating.[11]

We now design another approach to obtain copolymers with higher molecular weight and control of their structure in the zwitterionic copolymerization initiated by mixing donor and acceptor monomers. Since low molecular weight polymer is assumed to be caused by a β-proton transfer reaction from an unstable cation site of the zwitterion, the cation of the zwitterion should be protected by a nucleophilic counteranion like living cationic polymerization of vinyl ether in the HI/I_2[12] or ZnX_2[13] systems. Although the anion site of the zwitterion is anticipated to undergo less side reaction than the cationic site because of a rare hydride transfer reaction, the counter metal cation of the anion is known to assist the anionic chain-transfer reaction,[14] and hence the gegencation of the anion of the zwitterion should be an ammonium cation like the living anionic polymerization of methyl methacrylate initiated by ammonium thiolate[14] or carbanion.[15] Accordingly, an increase of the molecular weight and control of the copolymer structure could be attained by adding ammonium halides into zwitterionic polymerization systems. Thus, polymerization would proceed by nucleophilic substitution of the anion site to the alkyl halide site of a genetic zwitterion to afford an alternating copolymer (Scheme 1).

In this paper, we report that only addition of ammonium halides into the zwitterionic polymerization system of 4-phenyl-2-methylene-1,3-dioxolane (1) and methyl α-cyanoacrylate (2) permits an increase of the molecular weight and control of the copolymer structure as alternating, although this spontaneous copolymerization without additive has been reported to afford a random copolymer with low molecular weight ($\bar{M}_n$ = 800).[4]

Scheme 1

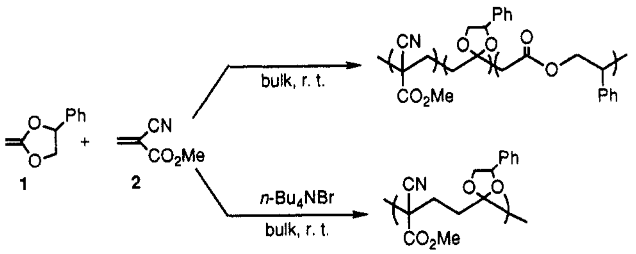


A: Electron-accepting monomer
D: Electron-donating monomer

Table 1. Copolymerization of 1 with 2 in the Presence of Ammonium Halide[a]

					copolymer		
entry	ammonium halide	solv[b]	temp, °C	time, h	yield,[c] %	composition[d] 1/2	mol wt[e]
1	TBAI[f]		25	96	78	44/56	2200
2	TBAI		60	44	74		920
3	TBAB[g]		25	72	98	46/54	5100
4	TBAB		60	25	60		1000
5	TBAB	DMF	25	96	58	47/53	2400
6	TBAB	DMF[h]	60	23	51		1000
7	TBAB	THF	25	96	61	49/51[i]	2400
8	TBAB	DME[j]	25	96	84	47/53	2300
9	TBAB	CH_3CN	25	96	71	48/52	800
10	TBAC[k]	THF	25	96	31[l]	19/81	730
11[m]		THF	25	12	35	45/55	800

[a] Copolymerization of equimolar 1 and 2 was carried out in the presence of 1.2 equiv of tetrabutylammonium halide. [b] $[1]_0 = [2]_0$ = 2 M. [c] Insoluble in hexane. [d] Estimated by ^1H NMR. [e] Determined by gel permeation chromatography by using three TSK gel columns (G-2000HXL, G-2500HXL, and G-3000HXL or G-2000HXL, G-4000HXL, and G-4000HXL) with THF eluent (based on polystyrene standards). [f] Tetrabutylammonium iodide. [g] Tetrabutylammonium bromide. [h] $[1]_0 = [2]_0$ = 3.3 M. [i] Composition estimated by elemental analysis was also 49/51. [j] 1,2-Dimethoxyethane. [k] Tetrabutylammonium chloride. [l] Purified by high-performance liquid chromatography. [m] Comparative data of ref 4.



The copolymerization of equimolar 1 and 2 was carried out by the slow addition of 2 into the mixture of 1 and 1.2 equiv of tetrabutylammonium halides. The polymers obtained were purified by precipitation in hexane.[16] Table 1 summarizes the results. 1:1 copolymers were obtained by using tetrabutylammonium iodide (TBAI) and bromide (TBAB), whereas the copolymer rich in 2 was obtained in the case of tetrabutylammonium chloride (TBAC), implying that the copolymerization with TBAC might involve the homopolymerization of 2 initiated by TBAC (entries 1–9 vs entry 10). The copolymerization with TBAB yielded a copolymer with a higher molecular weight compared to the copolymerization with TBAI (entry 1 vs entry 3). It should be noted that the molecular weight was 6.4 times higher in the copolymerization with TBAB than that without ammonium salt (entry 3 vs entry 11). In addition, the molecular weight decreased with increasing reaction temperature wheter using TBAI or TBAB (entry 1 vs entry 2, entry 3 vs entry 4, and entry 5 vs entry 6). This may

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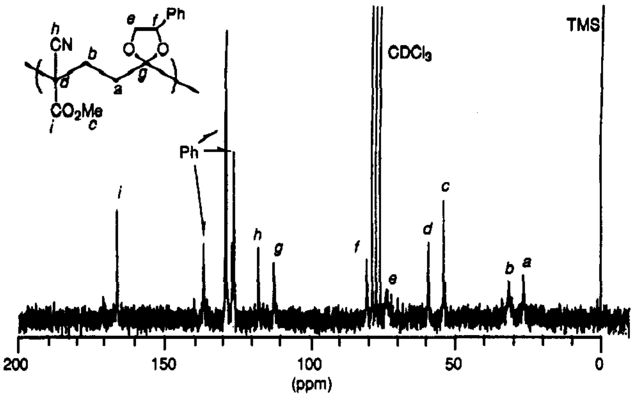
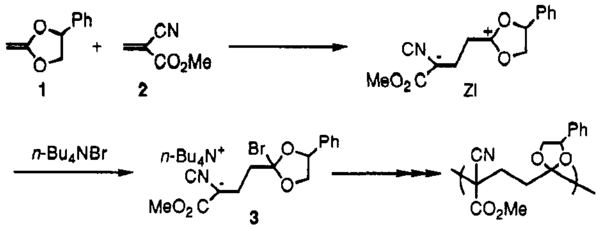


Figure 1. ^{13}C NMR spectrum of the copolymer of 1 and 2 in CDCl$_3$.

be ascribed to thermally induced Hofmann elimination of ammonium salts to generate proton and tributylamine which can terminate anionic and cationic reactions, respectively. Since the copolymerization with TBAB at 25 °C gave better results concerning the polymer yield and molecular weight, this copolymerization was carried out in various solvents (entries 5 and 7–9). Although 1:1 copolymers could be obtained in all cases, the molecular weights decreased compared to bulk polymerization.

^{1}H NMR spectra of the 1:1 copolymers showed the three signals of 1,3-dioxolane ring protons at 5.87–5.30, 4.87–4.40, and 4.17–3.47 ppm, and ^{13}C NMR spectra showed the characteristic signal due to the acetal carbon at 112.2 ppm, indicating that 1 copolymerized without ring opening. Although it has been reported that the ^{13}C NMR spectrum of the homopolymer of 1 without ring opening shows the backbone methylene carbon at 45 ppm,[17] there was no signal around 45 ppm in the ^{13}C NMR spectra of the 1:1 copolymer obtained with TBAB (Figure 1). Furthermore, the signal assigned to the backbone methylene carbon of the homopolymer of 2 at 43 ppm was not able to be observed, either. Instead of these signals of the backbone methylene carbons of the homopolymers of 1 and 2, ^{13}C NMR spectra of the 1:1 copolymer showed two different signals corresponding to two different backbone methylene carbons at 31.7 and 26.7 ppm and only one signal of carbonyl carbon. These observations indicate that the 1:1 copolymer is a head-to-head alternating copolymer of units from 1 without ring opening and 2. Furthermore, the ^{13}C NMR spectrum of the copolymer was in fair agreement with that of the head-to-head alternating copolymer of 1 and ethyl α-cyanoacrylate, which was obtained by the cationic ring-opening polymerization of the adduct between 1 and ethyl α-cyanoacrylate,[18] except signals of the ethyl group.

The production of a relatively high molecular weight alternating copolymer of 1 and 2 would be attributed to quantitative formation of bromo-substituted anion 3 under the following conditions satisfied. Thus, in the slow addition of 2 into the solution of 1 and TBAB, 2 may react with 1 faster than TBAB to afford zwitterion (ZI); otherwise, homopolymerization of 2 would be initiated by TBAB. Toward the cation site of ZI, bromide ion would react faster than 1 to yield 3; otherwise, homopolymerization of 1 would be initiated by the cationic site of ZI. Since these homopolymerizations of 1 and 2 could not be depressed, the random copolymer including homosequence of 1 and 2 might be obtained in the copolymerization without ammonium salts.



In summary, the present work may be the first example where the copolymer structure can be controlled and the molecular weight can be improved only by addition into the donor–acceptor zwitterionic copolymerization systems. Thus, an alternating copolymer of 1 and 2 with a high molecular weight could be obtained by addition of TBAB into the zwitterionic copolymerization system, although their spontaneous copolymerization without TBAB afforded a low molecular weight random copolymer.

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(16) Polymerization was carried out under dry argon in baked Schlenckware. Tetrabutylammonium halide (1.2 mmol) was placed in the Schlenckware and dried under reduced pressure for 1 h. A solution of 1 (1.0 mmol) in dichloromethane (1.5 mL) was injected into the flask and cooled to −78 °C, and then a solution of 2 (1.0 mmol) in dichloromethane (1.5 mL) was added slowly. After 20 min at that temperature, the reaction mixture was allowed to warm to room temperature, and dichloromethane was removed at reduced pressure. In bulk polymerization, the residue was allowed to stand for an appropriate time. In solution polymerization, the solvent was added into the residue and the mixture was stirred for an appropriate time. After quenching with methanol, the solvent and methanol were removed in vacuo, and the residue was dissolved by acetone–DMF (2:1) cosolvent (4 mL). The solution was poured into water (60 mL) (in order to remove ammonium salt) to give the precipitate, which was purified by dissolution

in dichloromethane (2 mL), followed by reprecipitation with hexane (40 mL). The polymer obtained was dried under reduced pressure or lyophilized with benzene: IR (neat) 2957, 2248, 1758, 1436, 1256, 1093, 1049, 1027, 753, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.31 (s, 5H), 5.87–5.30 (br, 1H), 4.87–4.40 (br, 1H), 4.17–3.47 (br, 1H), 3.86 (s, 3H), 2.70–1.70 (br, 4H); ^{13}C NMR ($CDCl_3$) δ 166.2, 136.4, 128.9, 126.7, 126.1, 117.6, 112.2, 80.3, 73.7, 59.2, 54.0, 31.7, 26.7.

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