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Proton-transfer Polymerization of Acrylate Monomer Containing Two Carboxyl Groups for Synthesis of Branched Polymer

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Abstract

This paper reports proton-transfer polymerization of an acrylate monomer containing two carboxyl groups. The monomer was synthesized by reaction of DL-malic acid with acrylic anhydride in the presence of a catalytic amount of acryloyl chloride. The polymerization was carried out in the presence of tributylphosphine as an initiator at 100°C. The product was isolated as a fraction insoluble in a mixture of *n*-hexane and diethyl ether. The structure of the polymer was determined by the ^{1}H and ^{13}C NMR spectra, as well as IR spectrum to be the polyester having a phosphonium end group. The molecular weights were estimated by GPC analyses with water as an eluent using poly(ethylene glycol) standards, which were 5500 – 11200 with the polydispersities of 1.6 – 2.6. Based on the analytical data, the following zwitterionic mechanism is proposed. The first step is formation of phosphonium-carboxylate zwitterion species by reaction of the monomer with the initiator. Then, the propagation proceeds via the Michael-type addition between the zwitterion species, followed by the proton-transfer process to give the polymer having ester linkages. Based on the polymerization mechanism, proposed here, the carboxyl groups in the monomer and polymer are considered as the latent propagating species. Therefore, the branched structure of the obtained polymer can be assumed.

Introduction

Hyperbranched polymers, macromolecules with branched backbones, have recently attracted much attention due to their specific structures and their different properties compared to the linear analogues. The preparation of these polymers was mainly conceived as an extension of a well-known class of polymerization reactions, in which hyperbranched polymers are typically prepared by the step-growth polymerization of AB_x-type monomers [1,2]. The other way to hyperbranched polymers is the chain-addition polymerization of monomers containing both an initiating function and a propagating function in the same molecules [3]. This type of addition polymerization yields hyperbranched polymers as products of multiple polymerization reactions within one polymer molecule. Here, the polymerization reactions are initiated by both an added initiator and initiating functional groups which are present in the monomers. The different type of chain polymerization for the preparation of the hyperbranched polymers was achieved by ring-opening polymerization of cyclic carbamates via π-allylpalladium complex, termed as "multibranching polymerization" [4,5]. During the polymerization, the number of propagating ends increased with the progress of the polymerization, and consequently hyperbranched dendritic polymers were produced. Recently, we have reported that base-catalyzed proton-transfer polymerization of acrylate monomers **1** containing two hydroxy groups gave the hyperbranched polymers **2** (Scheme 1) [6,7]. The polymerization provided the new method for the synthesis of hyperbranched polymers by the chain-growth type polymerization. Triphenylphosphine and sodium hydride were employed as the initiators, which initiated the polymerization via the Michael-addition toward monomer, followed by the proton-transfer. The formed anions induced the propagation, giving rise to the polymers having the unit structures of poly(ester-ether)s. In the polymerization, the hydroxy groups can be

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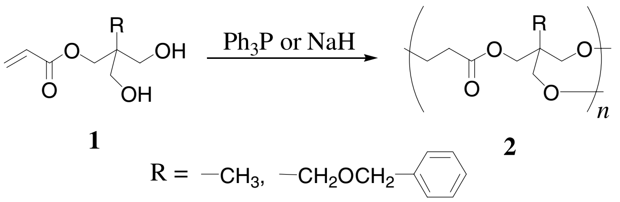
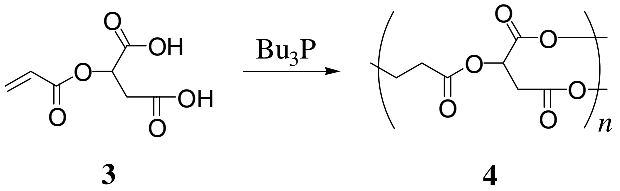
considered as the latent propagating species. The proton-transfer polymerization of **1**, therefore, gave the polymers with the hyperbranched structures.



Scheme 1

The base-catalyzed proton-transfer polymerization was not limited to the hydroxy-functionalized acrylate monomers such as **1**, but extended to carboxyl-functionalized acrylate monomers like acrylic acid [8]. The mechanism of the proton-transfer polymerization of acrylic acid has been reported as similar as that of **1**. We have examined, therefore, synthesis of branched-type polymer by the proton-transfer polymerization of acrylate monomer containing carboxyl groups. This paper reports the proton-transfer polymerization of a new acrylate monomer **3** containing two carboxyl groups for preparation of branched polymer **4** (Scheme 2).



Scheme 2

Experimental

Materials

Tributylphosphine was purified by distillation under reduced pressure. Acrylic anhydride was prepared according to the literature [9]. Other reagents and solvents were used as received.

Synthesis of Monomer 3

Under argon, a mixture of DL-malic acid (2.7 g, 20 mmol), acrylic anhydride (5.2 mL, 60 mmol), and a catalytic amount of acryloyl chloride (ca. 1 mmol) was heated at 90°C for 3 h. After cooling to room temperature, water (1.5 mL) was added to the mixture and the solution was stirred overnight at room temperature. The resulting solution was concentrated by evaporation and the residue was purified by column chromatography on silica gel with chloroform/methanol/formic acid (20:1:0.04) as the eluent to give **3** (2.6 g, 14 mmol) in 70.0% yield. ^{1}H NMR (D_2O): δ 3.05, 3.08 (2s, $CH_2C=O$, 2H), 5.48 (t, OCHC=O, 1H, *J* = 11.6 Hz), 6.02-6.56 (m, $CH_2=CH-$, 3H).

Polymerization of 3

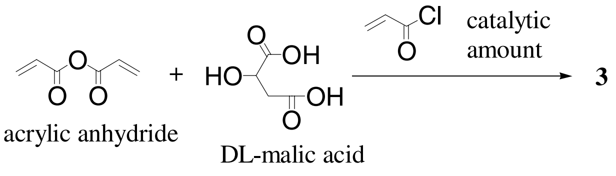
A typical polymerization was performed as follows (entry 3). Under argon, a mixture of **3** (0.14 g, 0.75 mmol), tributylphosphine (0.015 g, 0.075 mmol), and a small amount of *p*-methoxyphenol as a radical inhibitor was heated at 100°C. After 120 h, the product was treated with a small amount of 1 mol/L HCl aq. and dissolved in methanol (1 mL). The solution was poured into a mixture of *n*-hexane and diethyl ether (100 mL, 1:4 in volume) to precipitate the polymeric product. The polymer was isolated by decantation and dried in vacuo to give **4** (0.155 g, 21.8% yield).

Measurements

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded using a Varian INOVA 500 spectrometer. IR spectra were recorded on a HORIBA FT-720 spectrometer. Gel permeation chromatographic (GPC) analyses were performed by using a HITACHI L-7000 with an RI detector under the following conditions: TOSOH TSKgel G4000PW$_{XL}$ column with water as eluent at a flow rate of 1.0 mL/min. The calibration curve was obtained using poly(ethylene glycol) standards.

Results and Discussion

Monomer **1** was prepared by reaction of DL-malic acid with acrylic anhydride in the presence of a catalytic amount of acryloyl chloride (Scheme 3). The product was isolated by column chromatography on silica to give **3** in 70.0% yield. The structure of **3** was determined by the ^{1}H NMR spectrum.



Scheme 3

The polymerization of **3** was carried out with tributylphosphine as an initiator at 100°C for the desired reaction time. Other typical initiators for the proton-transfer polymerization such as triphenylphosphine, sodium hydride, and *t*-butanol were not effective compared with tributylphosphine. The reaction product obtained using tributylphosphine as the initiator was treated with diluted HCl aq. and precipitated into a mixture of *n*-hexane and diethyl ether (1:4) to isolate the polymer. The product polymer was soluble in high polar solvents like DMF and DMSO, but insoluble in lower polar solvents such as chloroform and toluene. The polymer structure was identified by means of ^{1}H NMR, ^{13}C NMR and IR spectra. Figure 1 shows the ^{1}H NMR spectrum of the polymer dissolved in DMSO-d_6. A new peak **c** at δ 4.22 assigned to the $CH_2OC{=}O$ appears (2H) compared with the ^{1}H NMR spectrum of **3**, indicating that the reaction proceeded by a Michael-type addition followed by a proton-transfer process giving a polymer having a unit structure **4**. As peaks for polymer focal units, the peaks **a** at δ 0.88, 1.41, and 2.18 assigned to the *n*-butyl protons of $(CH_3CH_2CH_2CH_2)_3P^+$ species are observed. Observation of these peaks indicates that the product polymer probably contained macrozwitterionic structure having $(CH_3CH_2CH_2CH_2)_3P^+$ end group. In addition to these signals, signals **b** and **d** appear at δ 2.4-3.0 and δ 5.23 assignable to $-CH_2C{=}O$ (4H) and $-OCH(C{=}O)C-$ (1H), respectively; peak **b** is overlapping with the DMSO peak. Furthermore, a small multiplet peaks ascribable to $CH_2{=}CHC{=}O$ are detected at δ 5.9-6.8, indicating that the product contains a small amount of gegenionic structure having the acrylate end group. The ^{13}C NMR spectrum of the same sample in Figure 2 exhibits peaks **a** at δ 12.7-25.6 due to $(CH_3CH_2CH_2CH_2)_3P^+$ end group, peaks **b** and **c** at δ 33.2 and δ 35.6, assignable to $\mathit{C}H_2C{=}O$, peaks **d** and **e** at δ 60.5 and δ 68.5 ascribable to $O{=}CO\mathit{C}H_2$ and $O\mathit{C}H(C{=}O)C$, and peaks **f** at δ 168.5-172.0 due to the carbonyl carbons. The IR spectrum of the polymer displayed strong absorption at 1739 cm^{-1} attributable to $\nu_{C=O}$ of the ester groups. These analytical results strongly suggest that the polymer has the unit structure of **4** obtained by propagation via the Michael-type addition and the subsequent proton-transfer process.

Table 1 summarizes the selected polymerization

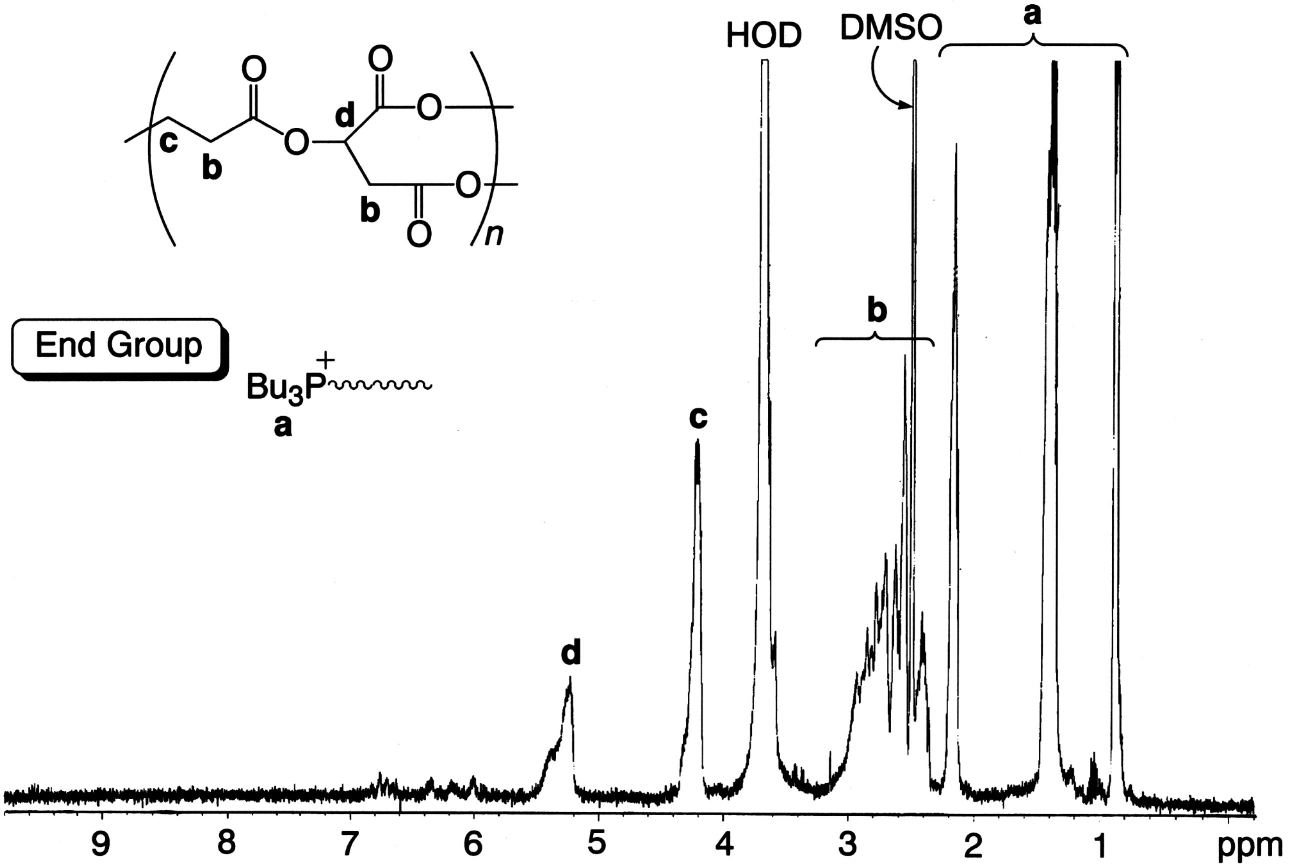


Fig. 1. ^{1}H NMR spectrum of the polymer (DMSO-d_6).

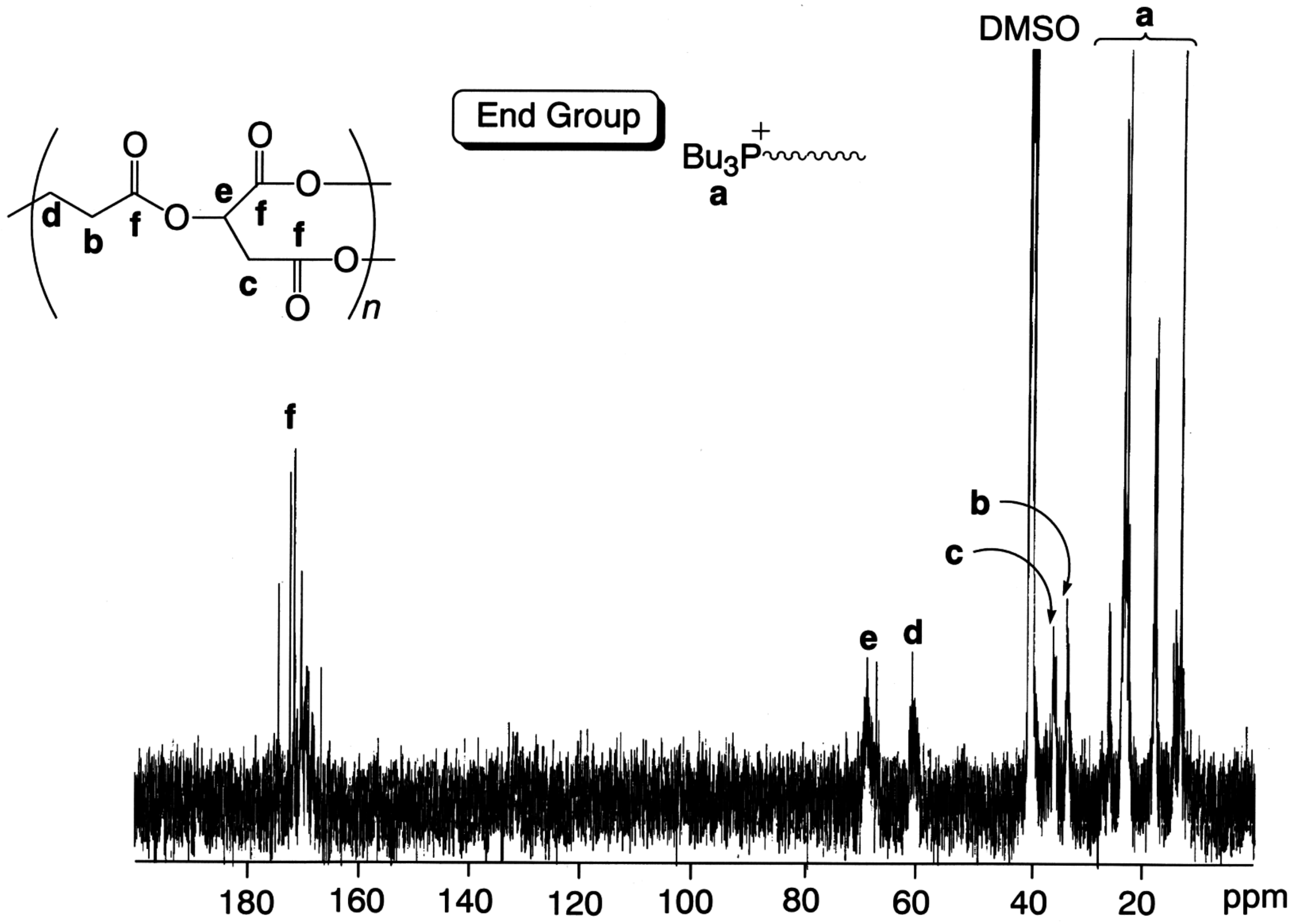


Fig. 2. ^{13}C NMR spectrum of the polymer (DMSO-d_6).

results under various conditions at 100°C. The values of the molecular weights (M_n), evaluated by means of GPC analysis with water as the eluent using poly(ethylene glycol) standards, were range of 5500-11200. There may be possibility for overestimation of M_n values by GPC measurements. Because, the M_n values determined by the integrated ratios of the peaks due to the polymer chains to the peaks due to $(CH_3CH_2CH_2CH_2)_3P^+$ end groups in the ^1H NMR spectra of the product polymers were always smaller than those estimated by the GPC measurement. Although the monomer conversions, determined directly from the ^1H NMR spectra of the reaction mixtures, were quantitative, the yields of the isolated polymers were not high. This indicates that the lower molecular weight fractions were lost during the isolation procedures by precipitation into a mixture of *n*-hexane and diethyl ether.

Table 1

Proton-transfer Polymerization of **3** Initiated with tributylphosphine at 100°C[a)]

Entry	Bu_3P (mol%)	time (h)	yield[b)] (%)	M_n[c)]	M_w/M_n[c)]
1	30	72	24.3	5500	1.9
2	30	96	29.8	6300	2.6
3	10	120	21.8	8500	2.1
4	20	120	26.8	9800	1.6
5	30	120	30.3	11200	1.6
6	30	168	21.8	6200	1.6

a) Monomer; 0.75 mmol (0.14 g), reaction temperature; 100°C.

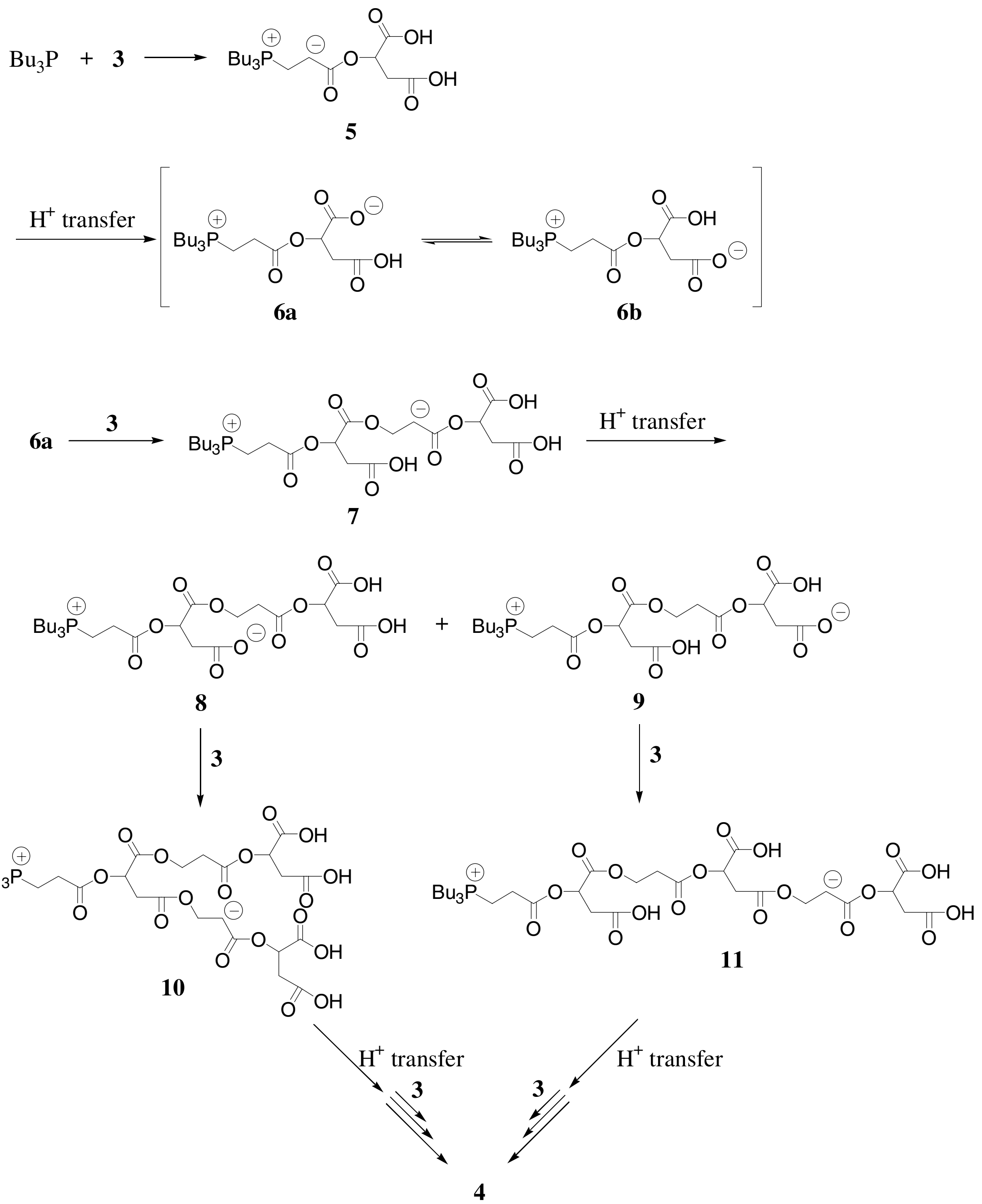
b) Fraction insoluble in a mixture of *n*-hexane and diethyl ether (1:4, v/v).

c) Determined by GPC with water as eluent using poly(ethylene glycol) standards.

Based on the data shown above, the following mechanism is proposed for the polymerization of **3** (Scheme 4). The first step is formation of the zwitterion **5** by the Michael-type addition of tributylphosphine onto **3**, followed by a proton-transfer process to give a zwitterion species **6**; there are two possibilities for the structures of the zwitterions **6a** and **6b**, due to the existence of two kinds of carboxyl groups. Then, the Michael-type addition of **6** (in

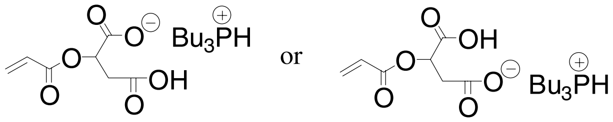
Scheme 4, **6a** is representatively described) onto **3** via the proton-transfer process occurs resulting in the dimeric zwitterion **8** or **9**. The Michael-type addition of **8** onto **3** produces the branched zwitterion **10**, whereas the addition of **9** onto **3** results in the linear zwitterion **11**. Then, the proton-transfer from unspecified carboxyl groups in **10** and/or **11** takes place to yield the trimeric zwitterions with various branched structures. Repetition of these reactions probably forms branched polymer **4** with macrozwitterionic structure. At the present time, the degree of branching (DB) is not yet clear. The most common definition is DB = (Br + Ter)/(Br + Li + Ter), where Br is the number of branching units, Li is the number of linear units, and Ter is the number of terminal units. The any analytical data of the products did not offer clues to calculate DB values. However, it can be assumed that the product polymers have some branched structures based on the above mechanism. The detailed study on the determination of the DB values are now in progress, which will be reported in the future.

The product polymer contains a small amount of



Scheme 4

the acrylate end groups in addition to the phosphonium end groups, as indicated in Figure 1. This indicates that the polymerization proceeded via not only the zwitterionic mechanism as shown in Scheme 4, but also gegenionic mechanism. At the initiation step, the genenionic species **12** may be partly formed by protonation of tributylphosphine from **3**, which also induced the propagation through the Michael-type addition followed by the proton-transfer process, giving the polymer with the acrylate end groups.



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Conclusions

Tributylphosphine-initiated proton-transfer polymerization of acrylate monomer **3** containing two carboxyl groups was carried out. The reaction proceeded via the Michael-type addition, followed by the proton-transfer process to produce the polymer **4** having the ester linkages. The unit structure of the polymer was confirmed by the ^{1}H, ^{13}C NMR and IR spectra. From the proposed mechanism as shown in Scheme 4, the branched structure of the polymer was assumed.

Acknowledgments

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