Macromol. Symp. ***183,*** *53–64 (2002)*

A New Type of Block Copolymerization with One-Shot Feeding of Two Monomers

Keigo Aoi [a], *Masatoshi Miyamoto* [b], *Yoshiki Chujo* [c], *Takeo Saegusa** [d]

Department of Synthetic Chemistry, Kyoto University, Kyoto 606-8501, Japan

Summary: This paper describes a new type of block copolymerization in which a block copolymer is produced with a "one-shot" feeding of monomers. The new block copolymerization is possible when the following prerequisites are met: (i) polymerization of two monomers proceeds via a living polymerization mechanism with a common initiator, (ii) the reactivities of the two monomers differ significantly from each other, and (iii) the propagating species of the monomer with higher reactivity is able to initiate the polymerization of the other monomer with lower reactivity. This new type of block copolymerization has been achieved by the combination of two monomers which were deliberately selected from among cyclic imino ethers. In addition, utilization of an oxazoline having a cyclic amine substituent at the 2-position as one component in the copolymerization has revealed another interesting phenomenon of this one-shot block copolymerization process, one involving "double isomerization polymerization". The new block copolymerization has conveniently been utilized in the preparation of surface-active agents having excellent performance.

Concept

This paper reports on a new type of block copolymerization with a "one-shot" feeding of two monomers. When a mixture of two monomers is subjected to polymerization, usually a random copolymer is produced. Sometimes an alternating copolymer or a mixture of the two homopolymers is formed. The new process that is the subject of this paper yields one block copolymer. The new block copolymerization was discovered in the course of research on the isomerization ring-opening polymerizations of cyclic imino ether monomers.

The new block copolymerization is different from conventional block copolymer

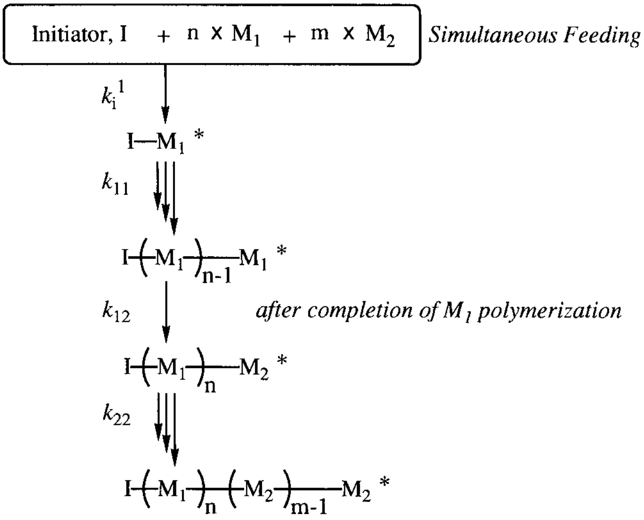
---

Current address: [a] Graduate School of Bioagricultural Sciences, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan; [b] Department of Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, Japan; [c] Department of Polymer Chemistry, Kyoto University, Kyoto 606-8501, Japan; [d] Professor Emeritus, Kyoto University, (Home) 8-22 Toji-in Kitamachi, Kita-ku, Kyoto 603-8346, Japan.

CCC 1022-1360/00/$ 17.50+.50/0

synthesis in which two monomers are introduced in a two-stage process to undergo polymerization. The new scheme is a special method which is possible under the following conditions: (i) the polymerizations of the two monomers proceed through a living polymerization mechanism with a common initiator, (ii) the difference in reactivity between the two monomers is large enough, and (iii) the living propagating species of the first monomer with the higher reactivity induces the polymerization of the second monomer with lower reactivity.

Scheme 1: General pattern of the new block copolymerization

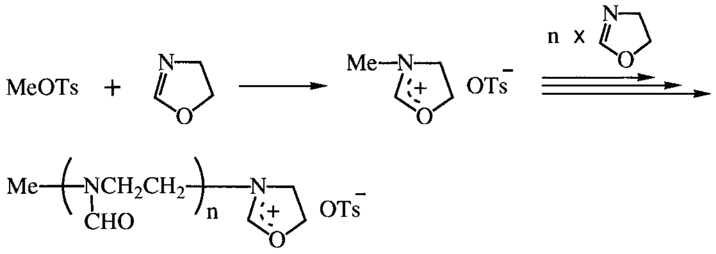


Scheme 1 illustrates the pattern of the new copolymerization. A ternary mixture of the initiator and two monomers M_1 and M_2 is fed in the reaction system. Then, monomer M_1 with higher reactivity is first polymerized in the presence of the second monomer M_2 with lower reactivity. After completion of the first monomer's polymerization, polymerization of the second monomer begins from the propagation end of the first monomer. For this scheme, the necessary relationships among rate constants of the initiations, k_i^1 and k_i^2, the homopropagations, k_{11} and k_{22}, and the cross propagation, k_{12}, are as follows:

$$k_i^1 > k_{11} >> k_i^2$$
$$k_{11} >> k_{12} > k_{22}$$

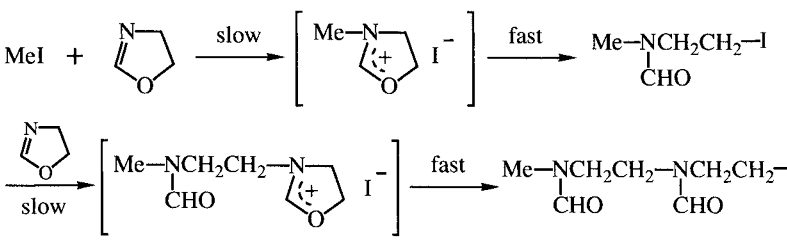
Before describing examples of this new block copolymerization, it will be useful to explain the polymerization mechanisms of cyclic imino ethers. It has been established that oxazoline is polymerized via one of two different propagating species, depending upon the nucleophilic reactivity of the counter anion derived from the initiator.[1,2] The first mechanism involves propagation via an ionic oxazolinium species (Scheme 2). The polymerization initiator, which is an electrophile, reacts with the monomer to produce the oxazolinium ion. When the counter anion derived from the initiator is less nucleophilic than the oxazoline monomer, the opening of the cyclic oxazolinium ion results from nucleophilic attack by another monomer molecule. This process then reiterates to constitute the propagation.

Scheme 2: Propagation via ionic propagating species (polymerization of unsubstituted oxazoline by methyl tosylate)



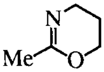
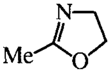
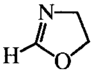
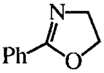
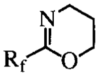
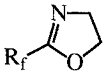
The second mechanism takes place when the counter anion from the initiator is more nucleophilic than the oxazoline monomer (Scheme 3). The propagation proceeds via a covalent nucleophilic species, in which the transient oxazolinium ion is opened via attack by the stronger nucleophile, the counter anion. According to the classic scheme of "cationic

Scheme 3: Propagation via covalent propagating species (polymerization of unsubstituted oxazoline by methyl iodide)



polymerization", the corruption of the cationic propagating species with the counter anion to form a covalent bond corresponds to "termination". However, in the polymerization of oxazoline, the covalent species proceeds to react with the monomer, and propagation continues. The rate determining steps in the two mechanisms are an ion/dipole reaction and a dipole/dipole reaction, respectively.

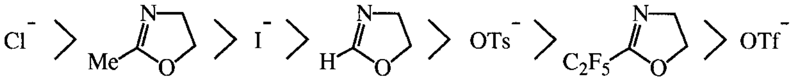
Table 1. Type of propagating species in the polymerization of cyclic imino ethers[a)]

M	Nucleophilicity ⟸					
X$^-$						
Cl$^-$	C	C	C	—	—	—
I$^-$	I	I	C	C	C	C
TsO$^-$	I	I	I	I	C	C
TfO$^-$	I	I	I	I	I	I

[a)] I = ionic species, C = covalent species.

Based on a series of kinetic as well as spectroscopic analyses for the polymerization of a family of cyclic imino ethers monomers with four initiators, the nature of the propagating species in the polymerization has been characterized as shown in Table 1.[3] Also, the order of the nucleophilic reactivities of monomers and of counter anions has been established as shown in Chart 1.

Chart 1: Comparison of nucleophilic reactivities of monomers and counter anions



Results and discussion

One-Shot Block Copolymerization between 2-Methyl-2-oxazoline (MeOZO) and 2-(Heptafluoropropyl)-2-oxazoline (C_3F_7OZO) with Methyl p-*nitrobenzenesulfonate Initiator*[4]

The copolymerization was carried out in nitromethane at 120 °C. The time/conversion curve is shown in Figure 1, which demonstrates the pattern of the rapid conversion of MeOZO (100% conversion in less than 2 minutes) and the subsequent slow conversion of the second monomer of C_3F_7OZO. Figure 2 shows gel permeation chromatography (GPC) curves of the two products after 2 minutes and after 40 hours, in which the block copolymer formation is clearly indicated. From ^1H NMR and ^{19}F NMR analyses as well as F content analysis, the first product after 2 minutes was found to be a homopolymer of MeOZO (no F atoms) and the

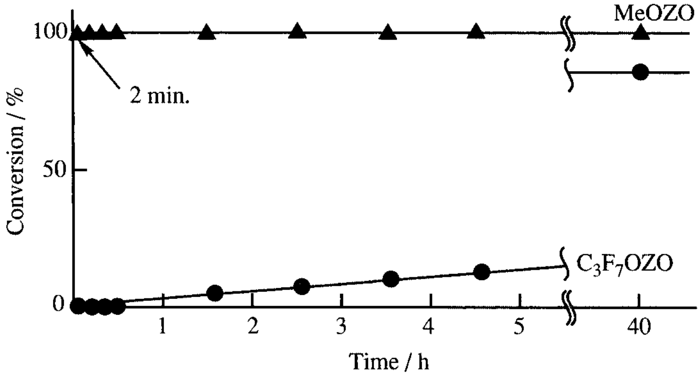


Figure 1. Time-conversion curves of "one-shot" block copolymerization between MeOZO and C_3F_7OZO ($[MeOZO]_0 = 2.64$ mol/L, $[C_3F_7OZO]_0 = 1.63$ mol/L, $[\text{methyl } p\text{-nitrobenzenesulfonate}]_0 = 0.52$ mol/L, $MeNO_2 = 0.8$ mL, at 120 °C).

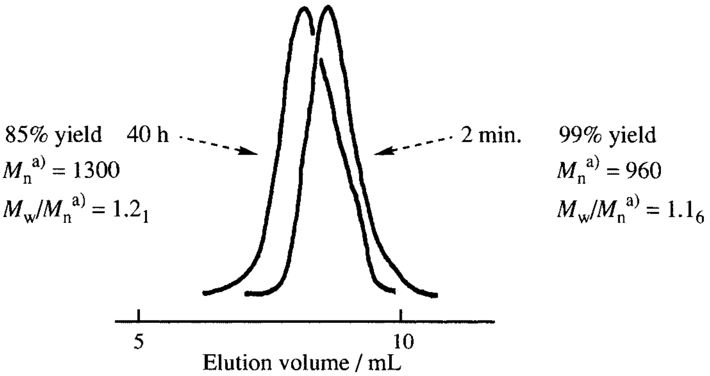
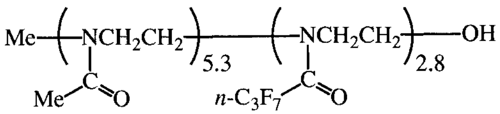


Figure 2. GPC curves of the products prepared in Figure 1.
[a)] Estimated by GPC with a calibration curve of standard poly(2-methyl-2-oxazoline).

second product after 40 hours was a block copolymer having the structure proposed in Chart 2.

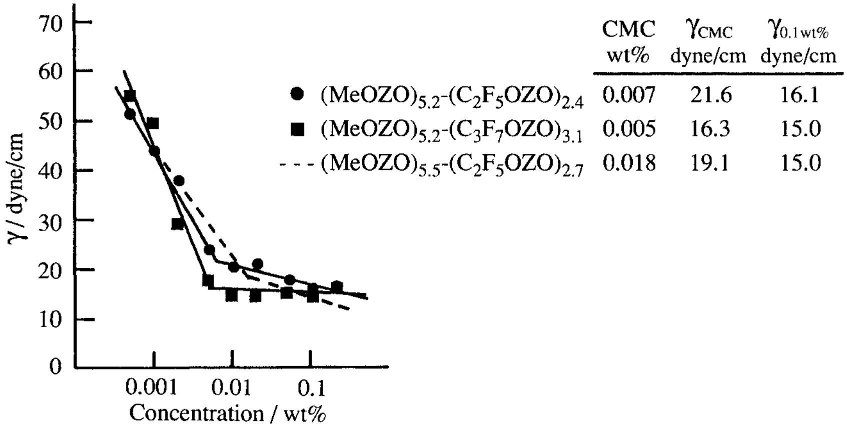
Chart 2: Structure of block copolymer of MeOZO and C_3F_7OZO



$$\mathrm{Me}-\left(\mathrm{N(C(=O)Me)CH_2CH_2}\right)_{5.3}-\left(\mathrm{N(C(=O)}\text{-}n\text{-}\mathrm{C_3F_7)CH_2CH_2}\right)_{2.8}-\mathrm{OH}$$

In comparison with MeOZO, the reactivity of C_3F_7OZO is much lower due to the strong electron-withdrawing effect of the perfluoropropyl group. Thus, MeOZO polymerization can proceed to completion before C_3F_7OZO polymerization begins. In this reaction, it is interesting to note that the propagating species of the C_3F_7OZO polymerization was a covalent species of *p*-nitrobenzenesulfonate esters. Previous studies have shown that electrophilic polymerization of 2-(perfluoroalkyl)-2-oxazoline proceeds via such covalent species with sulfonate initiators.[5]

The block copolymer prepared after 40 hours of heating was water-soluble and its solution showed an excellent surface tension value (as low as 17.1 dyne/cm at 0.1 wt.-%). The cloud point was higher than 100 °C. Figure 3 shows the surfactant properties of similar block copolymers prepared by the same process. The varying composition of the block copolymers were a function of the starting molar ratios of MeOZO to perfluoroalkyl oxazoline.



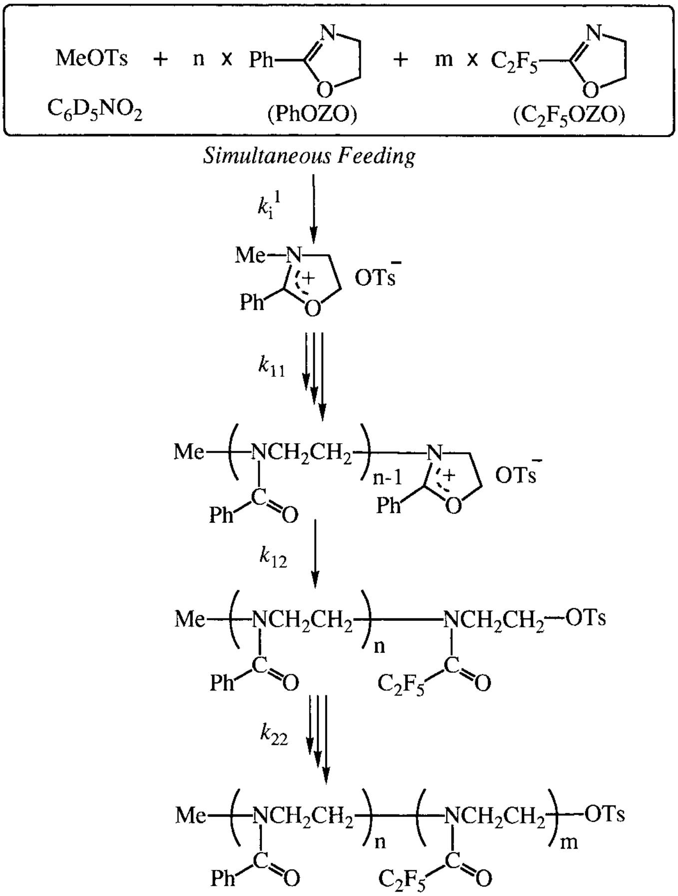
	CMC wt%	γ_{CMC} dyne/cm	$\gamma_{0.1\,wt\%}$ dyne/cm
● $(MeOZO)_{5.2}$-$(C_2F_5OZO)_{2.4}$	0.007	21.6	16.1
■ $(MeOZO)_{5.2}$-$(C_3F_7OZO)_{3.1}$	0.005	16.3	15.0
- - - $(MeOZO)_{5.5}$-$(C_2F_5OZO)_{2.7}$	0.018	19.1	15.0

Figure 3. Surfactant properties of MeOZO/perfluoroalkyl oxazoline block copolymers prepared by "one-shot" process (●, ■) and by conventional one-pot two-stage feeding process (- - -). CMC means critical micelle concentration.

One-Shot Block Copolymerization between 2-Phenyl-2-oxazoline (PhOZO) and 2-(Pentafluoroethyl)-2-oxazoline (C_2F_5OZO)—Kinetics[4]

Kinetic analysis of the copolymerization between PhOZO and C_2F_5OZO with methyl tosylate as initiator was carried out using perdeutero-nitrobenzene ($C_6D_5NO_2$) as solvent. The proposed mechanism for this copolymerization is shown by the series of reactions in Scheme 4.

Scheme 4: One-shot block copolymerization between PhOZO (M_1) and C_2F_5OZO (M_2)



The time/conversion curves for the initiator and PhOZO at the first stage temperature of 60 °C were constructed by means of ^1H NMR analyses. For the propagating species and

C_2F_5OZO at the second stage temperature of 150 °C, the time/conversion curves were traced by ^1H NMR and by ^{19}F NMR, respectively (Figure 4). From the data it was observed that PhOZO polymerization was complete after 12 hours at 60 °C. At this point the temperature of the mixture was increased to 150 °C and polymerization of C_2F_5OZO began.

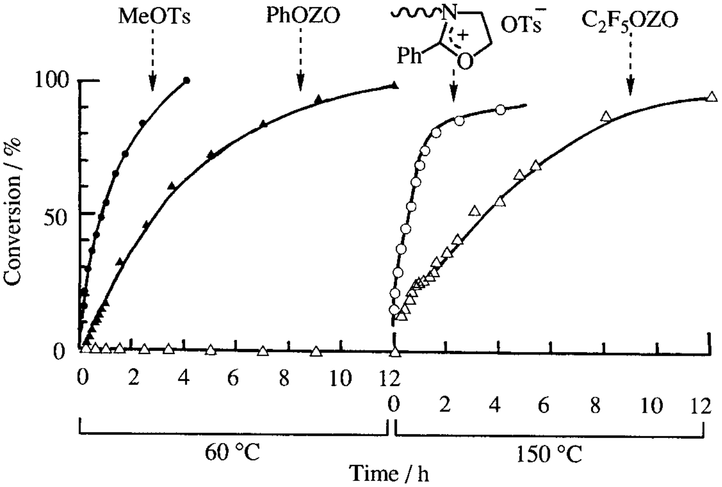


Figure 4. Time-conversion curves of four species in "one-shot" feeding with two-stage heating ($[PhOZO]_0$ = 3.19 mol/L, $[C_2F_5OZO]_0$ = 1.79 mol/L, [methyl tosylate]$_0$ = 0.624 mol/L, in $C_6D_5NO_2$).

The rate constant values of the polymerizations of PhOZO at 60 °C and C_2F_5OZO at 150 °C were determined by a procedure described previously.[4] The values are shown in Table 2. At 60 °C, the rate constant for polymerization of PhOZO is higher by an estimated magnitude of 3 compared to the rate constant for initiation of polymerization of C_2F_5OZO.

Table 2. Kinetic rate constants in the one-shot block copolymerization of MeOZO (M_1) and C_2F_5OZO (M_2) with methyl tosylate in $C_6D_5NO_2$

	k_i^1 L/(mol·s)	k_{11} L/(mol·s)	k_{12} L/(mol·s)	k_{22} L/(mol·s)
Temp = 60 °C	4.23 x 10^{-5}	4.10 x 10^{-5}	1 x 10^{-8} a)	
Temp = 150 °C			4.77 x 10^{-4}	9.13 x 10^{-5}

a) Calculated from the conversion of C_2F_5OZO after 48 h.

This kinetic analysis supports the pattern in Scheme 4 for the block copolymerization with "one-shot" feeding of the two monomers.

GPC analysis of the product after the first heating at 60 °C and that of the second product at 150 °C shows the formation of a block copolymer (Figure 5). This pattern is similar to that seen in Figure 2.

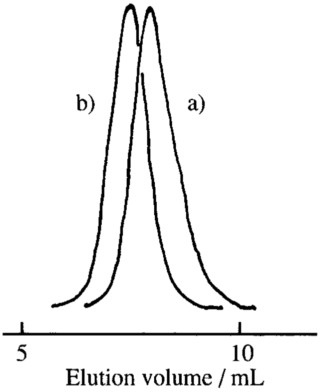
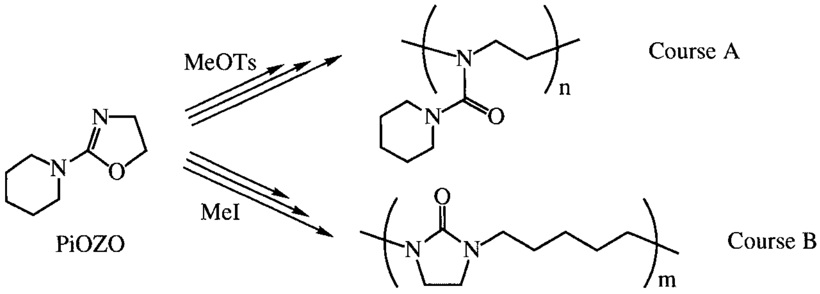


Figure 5. GPC curves of the products at 60 °C (a) and at 150 °C (b) in "one-shot" feeding with two-stage heating (The reaction conditions are given in Figure 4.).

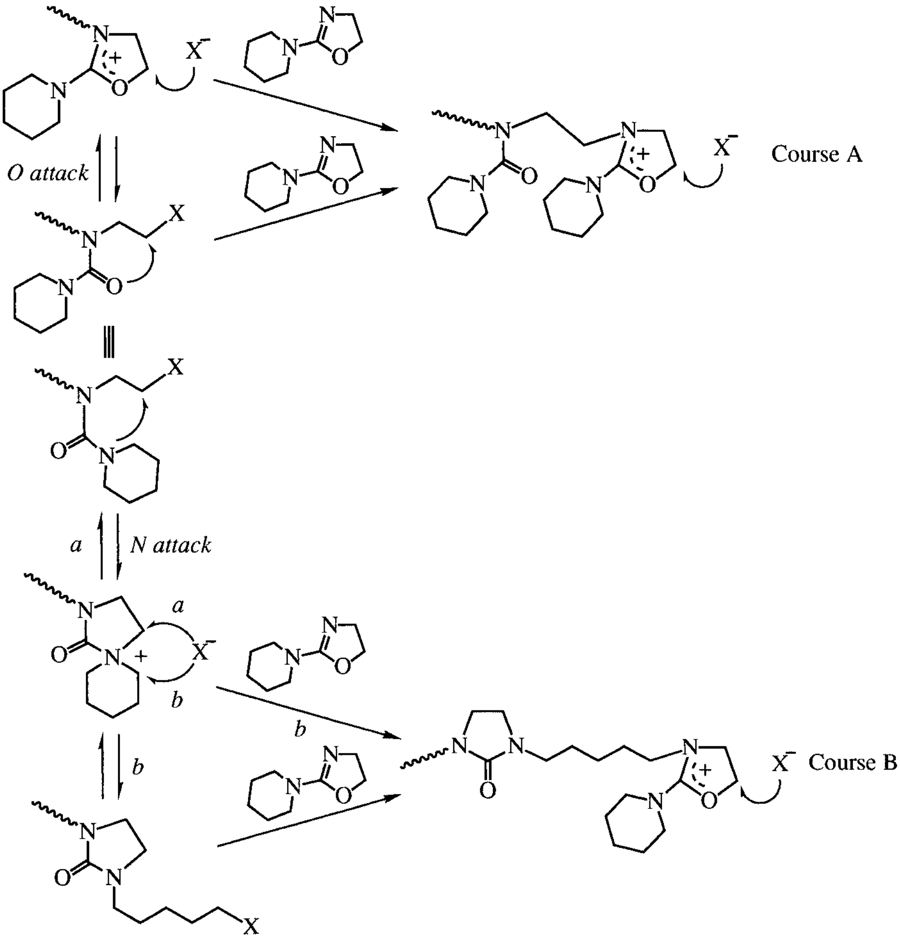
One-Shot Block Copolymerization between 2-Piperidino-2-oxazoline (PiOZO) and PhOZO

Previously, our study on the polymerization of a family of oxazolines has been extended to the polymerization of 2-imino-2-oxazoline, where an interesting phenomenon termed "Double Isomerization Polymerization (DIP)" was observed.[3,6] This phenomenon involves an "isomerization polymerization accompanying an isomerization of the propagating species". The pattern of polymerization of an oxazoline having a cyclic imino group at the 2-position is described in Scheme 5, where two courses of polymerization of a cyclic pseudourea, 2-piperidino-2-oxazoline, are shown. With methyl tosylate as initiator, the usual "single isomerization polymerization" takes place to produce poly-*N*-carbamoylethylenimine (Course A). On the other hand, with an alkyl halide initiator such as methyl iodide, the "double isomerization polymerization" occurs to produce a polymer of poly-alkyleneurea (Course B).

Scheme 5: Double isomerization polymerization of PiOZO



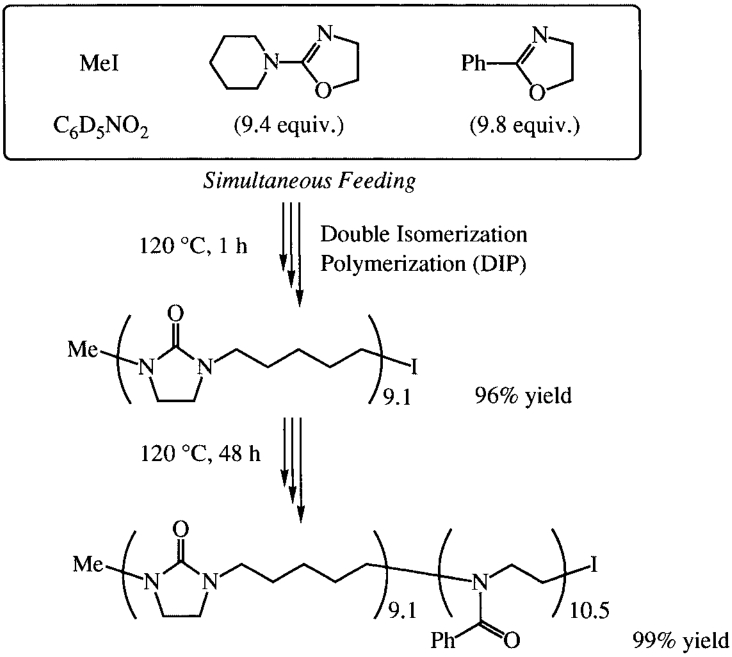
Scheme 6: Reaction pathways of double isomerization polymerization of 2-piperidino-2-oxazoline



The pathways of courses A and B are explained in Scheme 6. With an initiator generating a counter anion of lower nucleophilic reactivity compared to the oxazoline, the opening of the oxazolinium ring at the propagating end is caused exclusively by the nucleophilic attack of the monomer (Course A). With an initiator producing a counter anion of higher nucleophilic reactivity than the oxazoline, the reaction follows another pathway involving the following sequence: formation of a spiro-ammonium-type species, and the opening of the 6-membered cyclic amine by an intermolecular attack of the monomer or by attack of the counter iodide anion to convert to a covalent-type species (Course B).

With that as background, from the view point of one-shot block copolymerization, use of PiOZO as one of the monomers was of interest because of its relatively strong nucleophilic reactivity. The nitrogen atom in the oxazoline ring is at the position of tautomerism with the nitrogen atom of the 6-membered amine ring, and hence its nucleophilicity is reinforced. In combination with PhOZO, whose nucleophilic reactivity is rather weak (see Table 1), one-shot

Scheme 7: One-shot block copolymerization between PiOZO and PhOZO



block copolymerization of PiOZO took place with methyl iodide as initiator in $C_6D_5NO_2$ at 120 °C (Scheme 7). The course of polymerization was monitored by ^1H NMR and the block copolymer product was analyzed by GPC.

Double isomerization polymerization of PiOZO took place at 120 °C, nearing completion after 1 hour. The resulting covalent nucleophilic species then reacted with PhOZO over time to complete the copolymerization.

Conclusions

We have uncovered a new type of block copolymerization that involves one-shot feeding of two monomers rather than the standard two-stage process. Three prerequisites must be satisfied in order for successful copolymerization to occur. Using this method, we synthesized several block copolymers whose solutions possessed excellent surface tension values. It is our hope that this new block copolymerization can be further refined and put to beneficial use in a wide range of polymeric materials design.

[1] T. Saegusa, *Makromol. Chem.* **1974**, *175*, 1199.

[2] T. Saegusa, *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 111.

[3] T. Saegusa, K. Aoi, M. Miyamoto, Y. Chujo, *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 163.

[4] T. Saegusa, Y. Chujo, K. Aoi, M. Miyamoto, *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 1.

[5] M. Miyamoto, K. Aoi, T. Saegusa, *Macromolecules* **1991**, *24*, 11.

[6] M. Miyamoto, K. Aoi, S. Yamaga, T. Saegusa, *Macromolecules* **1992**, *25*, 5111.