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Synthesis of a Nonionic Polymer Surfactant from Cyclic Imino Ethers by the Initiator Method

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ABSTRACT: A nonionic polymer surfactant having a hydrophilic poly(*N*-acylalkylenimine) segment from a cyclic imino ether monomer has been synthesized, in which a hydrophobic group was introduced at the initiation stage of polymerization of the monomer ("initiator method"). Monomers used for construction of the hydrophilic segment are 2-methyl-, 2-ethyl-, and 2-*n*-propyl-2-oxazolines and 2-methyl-5,6-dihydro-4*H*-1,3-oxazine. Most of the product polymers are soluble in water, and their surfactant properties were evaluated by the surface tension (γ) of the aqueous polymer solution. Three methods to prepare the surfactants are described. (i) *n*-Octyl, *n*-dodecyl, and 2-(perfluorooctyl)ethyl trifluoromethanesulfonates (triflates) were employed for the fast initiation method, *n*-octyl tosylate being for fast initiation of the 1,3-oxazine monomer too. (ii) *n*-Dodecyl tosylate and α,ω-dodecamethylene bis(tosylate) were used for slow initiation of the 2-methyl-2-oxazoline polymerization. (iii) An *N*-methyl tosylate of 2-(higher alkyl)-2-oxazoline induced rapid polymerization of 2-oxazolines. Methods i and iii were found suitable for producing effective nonionic polymer surfactants. The γ value reached 23.9 dyn/cm for a polymer sample from 2-(perfluorooctyl)ethyl triflate/2-ethyl-2-oxazoline.

Introduction

Cationic ring-opening polymerization of cyclic imino ethers is conveniently used to prepare poly(*N*-acylalkylenimines), which are good starting materials for linear poly(alkylenimines). The polymerization is of highly living nature.[1] Very recently we reported the preparation of block copolymers utilizing the polymerization of cyclic imino ethers.[2] One-pot two-stage and one-pot three-stage copolymerizations afforded AB- and ABA- (or BAB) type block copolymers, respectively, in which A or B denotes a hydrophilic or lipophilic polymer chain. A bis-functional initiator also gave a BAB type block copolymer. These copolymers, e.g., a AB-type copolymer, possess both hydrophilic and lipophilic chains in the same molecule and,

$$-[N[C(=O)R_1]CH_2CH_2]_m-[N[C(=O)R_2]CH_2CH_2]_n-$$

hence, showed very good surfactant properties evaluated by the surface tension (γ) of copolymer in water. The properties arise from the fact that the *N*-acylethylenimine chain is hydrophilic when $R_1 = CH_3$ or C_2H_5, becoming lipophilic when $R_2 = C_4H_9$, a higher alkyl, or aryl group. These results suggested the synthesis of another type of a nonionic polymer surfactant, which is composed of a hydrophilic *N*-acylethylenimine chain and of a hydrophilic alkyl group such as *n*-octyl, *n*-dodecyl, or fluoroalkyl group. The hydrophobic group is introduced at the initiation stage ("initiator method"). In relation to the present study, dodecylbenzenesulfonyl chloride, poly(isobutylenesulfonyl chloride), brominated polyisobutylene, a variety of lipophilic initiators such as dodecylbenzyl chloride, octanoyl chloride, etc. were previously claimed as initiators for polymerizing 2-oxazolines, leading to another class of polymer surfactants.[3]

Results and Discussion

A cyclic imino ether monomer is employed to give a hydrophilic chain, and, hence, methyl, ethyl, and *n*-propyl groups are employed as an alkyl substituent. In this study the hydrophobic alkyl group is introduced by the initiation step of the polymerization of 2-alkyl-2-oxazolines. Three "initiator methods" have been investigated.

I. Fast Initiation Method. An alkyl trifluoromethanesulfonate (R_2OTf) is approximately 10^4 times more reactive in alkylation than the corresponding *p*-toluenesulfonate (ROTs).[4] Three kinds of R_2OTf [R_2 = *n*-octyl, *n*-dodecyl, and 2-(perfluorooctyl)ethyl] were employed for preparing nonionic polymer surfactant 2 from 2-methyl-, 2-ethyl-, and 2-*n*-propyl-2-oxazolines (MeOZO, EtOZO, and PrOZO, respectively) (Table I).

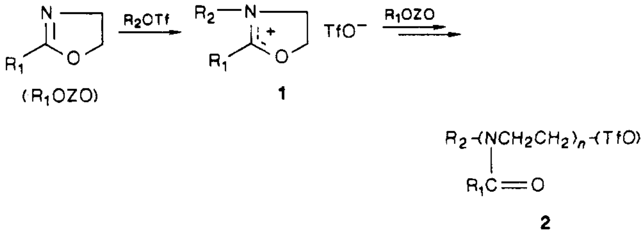

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Table I
Synthesis of Polymer Surfactant 2 from 2-Oxazolines with R_2OTf Initiator

entry	R_1	R_2	$[R_1OZO]_0/[R_2OTf]_0$	react time,[a] h	polymer 2 yield, %	 $\overline{DP}$ (n)[b]	 γ,[c] dyn/cm
1	CH_3	n-C_8H_{17}	2.6	6	77	2.6	32.9
2	CH_3	n-C_8H_{17}	4.4	6	97	3.3	33.5
3	CH_3	n-C_8H_{17}	5.6	14	93	6.4	29.6
4	CH_3	n-C_8H_{17}	9.0	18	99	10.0	31.2
5	CH_3	n-C_8H_{17}	13.7	18	99	12.8	31.7
6	C_2H_5	n-C_8H_{17}	2.9	24	84	3.6	32.0[d]
7	C_2H_5	n-C_8H_{17}	4.4	24	94	6.6	31.7[d]
8	C_2H_5	n-C_8H_{17}	9.9	33	100	10.9	37.2[d]
9	n-C_3H_7	n-C_8H_{17}	3.2	65	87	4.8	33.3[d]
10	n-C_3H_7	n-C_8H_{17}	5.5	65	94	6.3	34.0[d]
11	CH_3	CH_3	2.7	18	91	2.9	32.9
12	CH_3	n-$C_{12}H_{25}$	4.9	18	99	4.5	36.9
13	CH_3	n-$C_{12}H_{25}$	9.7	22	100	9.6	45.2
14	CH_3	$C_8F_{17}CH_2CH_2$	4.6	16	69	4.4	26.5
15	CH_3	$C_8F_{17}CH_2CH_2$	9.8	17	87	8.0	32.6
16	CH_3	$C_8F_{17}CH_2CH_2$	13.7	17	100	12.7	34.6
17	C_2H_5	$C_8F_{17}CH_2CH_2$	4.9	28	85	5.7	23.9
18	C_2H_5	$C_8F_{17}CH_2CH_2$	9.6	24	57	7.3	30.9

[a] Monomer (R_1OZO) = 4.0 mmol in 2.0 mL of CH_3CN at 80 °C under nitrogen. [b] From ^1H NMR analysis. [c] The surface tension (γ) was measured with a Du Noüy tensiometer with the polymer concentration = 1.0 wt %, which is higher than the critical micelle concentration at an ambient temperature and recalculated to the value at 20 °C (γ of water at 20 °C = 72.8 dyn/cm). [d] Measured with the concentration = 0.5 wt %. The sample polymer was partially insoluble.

This method is the most straightforward for the preparation of a nonionic polymer surfactant having a hydrophobic group and a hydrophilic polymer chain. In most cases the yield of polymer (oligomer) 2 is quantitative. The degree of polymerization ($\overline{DP}$) of 2 determined by ^1H NMR was always very close to the charged $[R_1OZO]/[R_2OTf]$ molar ratio. This is because the initiation to form 1 is very rapid and the subsequent propagation is slow. The M_w/M_n values obtained by gel permeation chromatography (GPC) were as follows: entry 5, 1.28; entry 8, 1.26; entry 13, 1.27; and entry 16, 1.28.

The surfactant properties of polymer 2 were evaluated by measuring the surface tension (γ) in water, because almost all polymer samples were soluble in water. All samples showed good surfactant properties; for example, sample 3 ($R_1 = CH_3$; $R_2 = n\text{-}C_8H_{17}$) exhibit γ values lower than 30 dyn/cm. It is to be noted that PrOZO gave an effective hydrophilic chain although polymers are not completely soluble in water (entries 9 and 10). A fluoroalkyl triflate produced polymers of high surfactant nature, e.g., γ = 23.9 dyn/cm of entry 17.

Figure 1 indicates the γ-value dependency with respect to the polymer concentration. The critical micelle concentration (cmc) of sample 14 is lower than 0.01 wt % whereas that of entry 3 is around 0.5 wt %, thus demonstrating the excellent performance characteristic of a fluoroalkyl group derived surfactant.

A characteristic of surfactants 2 from MeOZO and EtOZO is that they do not show a clouding point, e.g., 1.0 wt % aqueous solutions of samples 3, 6, 8, and 14 remained clear even at boiling (≥100 °C) of the solutions. This is probably due to a strong hydrogen bonding of water with amide groups of high polarity.[2] These observations are interesting for comparison with polyether-type polymer surfactants, poly(ethylene oxide) and poly(propylene oxide) block copolymers (Pluronics), which show a clouding point. The γ values of 1.0 wt % aqueous solutions of Pluronics are in the range 35–45 dyn/cm at 25–30 °C,[5] indicating the less effective surfactant properties in comparison with 2.

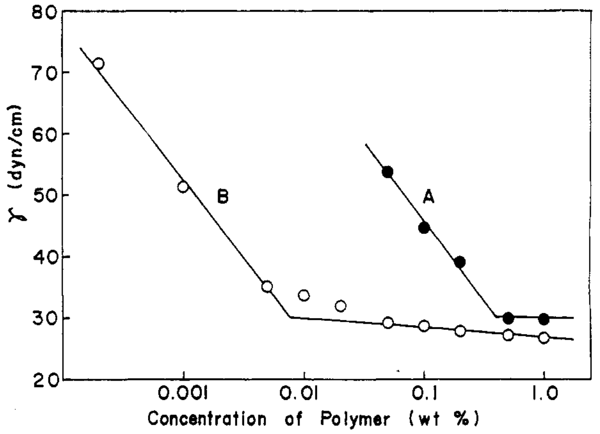
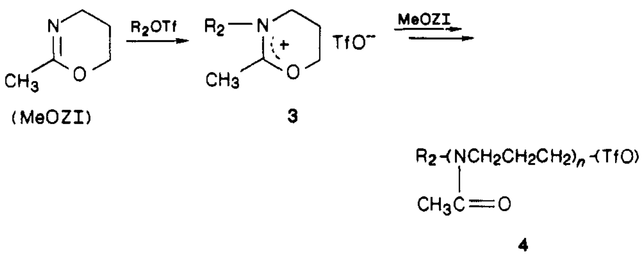


Figure 1. Relationships between polymer concentration and γ values: (A) sample 3; (B) sample 14.

2-Methyl-5,6-dihydro-4*H*-1,3-oxazine (MeOZI), a six-membered cyclic imino ether, was also employed for constructing a hydrophilic chain. n-Octyl and 2-(perfluorooctyl)ethyl triflates were used for the fast initiation of MeOZI via an onium salt (3) giving rise to polymer 4 (Table II). Again, $\overline{DP}$ determined by ^1H NMR analysis was always very close to the feed molar ratio [MeOZI]/[R_2OTf], indicating polymerization systems with rapid initiation and slow propagation. The M_w/M_n values are fairly small. The surfactant nature of 4 is very good in all cases as reflected by lower γ values.



Whether or not the polymerization system is of fast initiation depends upon the relative rate of initiation and propagation. The cationic ring-opening polymerization of MeOZI by MeOTs is known as a system of fast initiation and of slow propagation.[6] A simple comparison of the rate constant of initiation (k_i) and of propagation (k_p) reveals the ratio k_i/k_p = 20 with MeOTs initiator (Table III). Therefore, n-octyl tosylate (OcOTs) was used to polymerize

Table II
Synthesis of Polymer Surfactant (4) from MeOZI with R_2OTf Initiator

				polymer 4			
entry	R_2	$[MeOZI]_0/[R_2OTf]_0$	react time,[a] h	yield, %	$\overline{DP}$ (n)[b]	M_w/M_n[c]	γ,[d] dyn/cm
19	n-C_8H_{17}	3.0	24	87	2.9	1.33	32.9
20	n-C_8H_{17}	5.4	26	96	5.2	1.35	33.5
21	n-C_8H_{17}	9.4	28	99	8.2	1.32	34.2
22	$C_8F_{17}CH_2CH_2$	4.2	24	100	4.3	1.26	29.4
23	$C_8F_{17}CH_2CH_2$	6.1	24	100	6.0	1.26	29.6

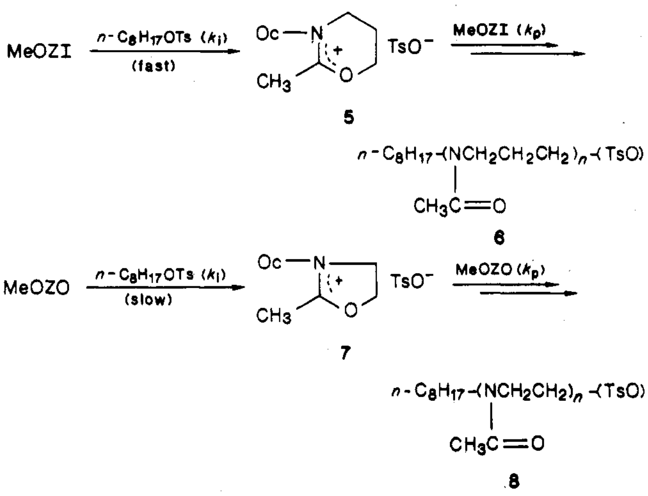
[a] Monomer, MeOZI = 4.0 mmol in 2.0 mL of CH_3CN at 80 °C under nitrogen. [b] From ^1H NMR analysis. [c] Determined by GPC. [d] Determined in a similar way as those in Table I.

Table III
Reactivities and Polymer Surfactant of MeOZI and MeOZO Using OcOTs Initiator

					polymer 6 or 8			
	k_i[a]	k_p[a]	entry	$[monomer]_0$[d]/ $[OcOTs]_0$	yield, %	$\overline{DP}$ (n)[e]	M_w/M_n[f]	γ,[g] dyn/cm
MeOZI	6.1[b]	(0.3)[b]	24	5.2	96	5.1	1.35	33.5
MeOZO	1.82[c]	1.17[c]	25	5.6	77	14.8	1.89	42.2

[a] ×10^4 L/mol s with MeOTs initiator. [b] Data at 35 °C in nitrobenzene.[6] The value in the parenthesis is a calculated value at 35 °C. [c] Data at 40 °C in CD_3CN.[7] [d] Monomer = 4.0 mmol in 2.0 mL of CH_3CN at 80 °C for 24 h under nitrogen. [e] Determined by ^1H NMR analysis. [f] Obtained by GPC. [g] Determined in a similar manner as those in Table I.

MeOZI for the preparation of surfactant **6**. The fast initiation to form onium salt **5** has been proved by entry 24, in which $\overline{DP}$ of **6** (5.1) is almost identical with the ratio



$[MeOZI]_0/[OcOTs]_0 = 5.2$. And the surfactant nature of **6** is good ($\gamma = 33.5$ dyn/cm).

A similar attempt using OcOTs as initiator was applied to the polymerization of MeOZO to prepare surfactant **8**. The ratio $k_i/k_p = 1.6$ is very small (Table III).[6] Taking the reactivity difference between MeOTs and OcOTs (at least several times)[4] into account, the OcOTs-initiated polymerization of MeOZO is expected to be a slow initiation but fast propagation system. As seen in entry 25, the $\overline{DP}$ of product polymer **8** is 14.8 with the feed ratio $[MeOZO]_0/[OcOTs]_0 = 5.6$, suggesting the slow production of **7** compared with propagation of MeOZO. Accordingly, M_w/M_n is relatively large and γ of **8** shows a lower surfactant property.

II. Slow Initiation Method. From the practical viewpoint, an alkyl tosylate is more readily accessible than a corresponding triflate. Therefore, n-dodecyl tosylate (DoOTs) was used to induce the cationic ring-opening polymerization of MeOZO leading to surfactant **9**, although the polymerization must be a slow initiation system (Table IV). All polymers **9** are soluble in water. The $\overline{DP}$ of **9**

$$\text{MeOZO} \xrightarrow{n\text{-}C_{12}H_{25}OTs} n\text{-}C_{12}H_{25}\text{-}[N[C(=O)CH_3]CH_2CH_2]_n\text{-}(TsO)$$
9

(n value) is in all cases larger than the $[MeOZO]_0/[DoOTs]_0$ ratio, indicating relatively slow initiation and fast propagation as seen in the preparation of polymer **8**. Even in the case of a large initiator amount of 50 mol % the $\overline{DP}$ reached $n = 13.6$. The γ values did not reach below 41.5 dyn/cm at 20 °C.

Table IV
Polymerization of MeOZO with *n*-Dodecyl Tosylate[a]

		polymer 9		
entry	$[MeOZO]_0/[DoOTs]_0$	mol wt[b]	$\overline{DP}$ (n)[c]	γ, dyn/cm[d]
26	40.0	4120	44.6	48.5
27	10.2	2420	24.6	46.8
28	3.80	1700	16.1	43.0
29	2.00	1490	13.6	41.5

[a] MeOZO = 15.0 mmol in 5.0 mL of CH_3CN at 80 °C for 15 h under nitrogen. The yield of polymer **9** was almost quantitative in all runs. [b] Determined by VPO. [c] Calculated from the molecular weight by VPO based on the structure **9**. [d] Obtained in a similar manner as those in Table I.

An extension of this method has been made to employ a bis-functional initiator. α,ω-Dodecamethylene bis(tosylate) (**10**) was used to initiate the MeOZO polymerization. With the use of 8.0 mol % of **10**, MeOZO polymer **11** was obtained in 84% yield. The average molecular weight of

$$\text{MeOZO} \xrightarrow{TsO(CH_2)_{12}OTs\ (10)} (TsO)\text{-}[CH_2CH_2N[C(=O)Me]]_m\text{-}(CH_2)_{12}\text{-}[N[C(=O)Me]CH_2CH_2]_n\text{-}(TsO)$$
11

11 was 2500 by VPO, leading to $m + n = 23.4$. This again indicates the slow initiation relative to the propagation rate. Polymer **11** is soluble in water and its γ value was 42.3 dyn/cm (20 °C), in which the dodecamethylene group acts as a lipophilic group. This surface-active property of **11** is comparable to that of polymer **9**.

Thus, the slow initiation method does not allow one to control the molecular weight of product polymers, which makes it harder to produce the polymers of the optimal hydrophilic–lipophilic balance (HLB). A previous claim using an alkyl halide initiator is also a slow initiation system and hence may have encountered the similar problem.[3]

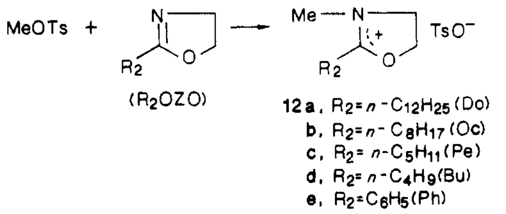
III. Isolated Salt Initiator Method. In order to overcome the problem of slow initiation using alkyl tosylates, we have prepared an oxazolinium tosylate species having

Table V
Polymerization of R_1OZO Initiated by Salt 12[a]

			polymer 13				
entry	$[R_1OZO]_0$/[salt $12]_0$	R_1 of monomer	yield, %	structure	mol wt (by VPO)	$\overline{DP}$ (n)[b]	γ,[c] dyn/cm
30	**12a**, 43.5	CH_3	100	**13a**	4540	48.4	48.1
31	**12a**, 24.4	CH_3	95	**13a**	2670	26.4	48.9
32	**12a**, 15.6	CH_3	95	**13a**	1810	16.3	48.6
33	**12a**, 11.0	CH_3	97	**13a**	1490	12.5	48.2
34	**12a**, 5.8	CH_3	89	**13a**	1020	7.0	43.5
35	**12a**, 11.4	C_2H_5	100	**13b**	1640	12.3	38.4
36	**12a**, 10.4	n-C_3H_7	97	**13c**	1520	9.7	insol
37	**12b**, 32.2	CH_3	97	**13d**	3220	33.5	44.1
38	**12b**, 22.2	CH_3	97	**13d**	2270	22.3	41.1
39	**12b**, 11.0	CH_3	96	**13d**	1400	12.1	33.9
40	**12b**, 5.6	CH_3	95	**13d**	970	7.1	33.1
41	**12c**, 9.3	CH_3	95	**13e**	1150	9.7	52.5
42	**12d**, 31.2	CH_3	100	**13f**	2990	31.5	63.8
43	**12d**, 20.8	CH_3	100	**13f**	2280	23.1	62.8
44	**12d**, 10.4	CH_3	100	**13f**	1350	12.2	56.7
45	**12d**, 5.3	CH_3	100	**13f**	830	6.1	59.0
46	**12e**, 9.9	CH_3	100	**13g**	1380	12.3	59.0

[a] Monomer (4.4 mmol) in 1.5 mL of CH_3CN at 80 °C for 30 h under nitrogen. [b] Calculated from the molecular weight by VPO based on the structure 13. [c] Determined similarly to those in Table I.

a lipophilic group for initiator. The following five 2-oxazolinium tosylates **12** have been prepared by the reaction of an excess amount of MeOTs with five 2-substituted-2-oxazolines (R_2OZO) and isolated as white solids.



Then, the isolated salt **12** was employed to induce the polymerization of 2-substituted-2-oxazoline (R_1OZO) giving rise to a designed polymer **13**.

$$12 \xrightarrow{R_1OZO} R_2C(=O)N(Me)CH_2CH_2\text{-}[N[C(=O)R_1]CH_2CH_2]_n\text{-}(TsO)$$

13a: $R_2 = n\text{-}C_{12}H_{25}$; $R_1 = CH_3$
13b: $R_2 = n\text{-}C_{12}H_{25}$; $R_1 = C_2H_5$
13c: $R_2 = n\text{-}C_{12}H_{25}$; $R_1 = n\text{-}C_3H_7$
13d: $R_2 = n\text{-}C_8H_{17}$; $R_1 = CH_3$
13e: $R_2 = n\text{-}C_5H_{11}$; $R_1 = CH_3$
13f: $R_2 = n\text{-}C_4H_9$; $R_1 = CH_3$
13g: $R_2 = C_6H_5$; $R_1 = CH_3$

Polymerization results are given in Table V. In all cases polymer yields were almost quantitative and the $\overline{DP}$ (n value) of polymer **13** is close to the feed $[R_1OZO]_0$/[salt $12]_0$ ratio. These can be taken to support that the polymerization of R_1OZO by salt **12** is a "fast initiation" system. *N*-Acetylethylenimine and *N*-propionylethylenimine chains are good hydrophilic groups. All polymers **13** containing either of the chains are soluble in water. But, polymer **13** having an *N*-butyrylethylenimine chain is not soluble in water. In entries 30–34 of the dodecyl group systems, polymer **13a** having the shortest chain length showed the best surfactant properties reflected by γ values. As a lipophilic group, *n*-butyl, *n*-pentyl, and phenyl groups are not suitable; the polymers **13e**, **13f**, and **13g** are probably too hydrophilic. Among polymers prepared, polymer **13d** (no. 40) of the *n*-octyl group exhibited the lowest γ value of 33.1 dyn/cm. As a whole, the longer chain length in polymer **13** does not increase the surfactant properties. Appropriate hydrophilic–lipophilic balance (HLB) may be achieved when the chain length is shorter than ca. 15 ($n < \sim 15$). With fixing the chain length $n \sim 12$, the nature of the lipophilic group is examined as a function of carbon number of the alkyl group with γ values (Figure 2), *n*-octyl group being the most suitable among R_2 groups examined.

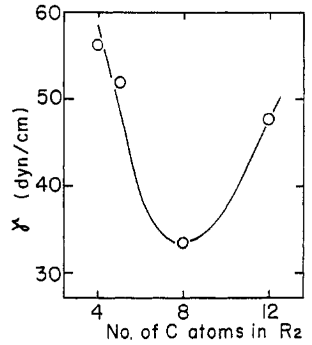


Figure 2. Relationships between γ value and the chain length of alkyl group R_2 of **13** with $n = \sim 12$.

Experimental Section

Materials. Solvents, CH_3CN, pyridine, and diethyl ether, were purified in a usual manner. Commercial reagents of MeOZO (Aldrich Chemical Co.) and EtOZO (gift from Dow Chemical Co.) were purified by distillation. Monomers, PrOZO, BuOZO, PeOZO, OcOZO, DoOZO, PhOZO, and MeOZI were prepared according to the literature.[8] A commercial reagent of MeOTs was purified by distillation. Commercial reagents, 1-octanol, 1-dodecanol, 1,12-dodecanediol, *p*-toluenesulfonyl (tosyl) chloride, and trifluoromethanesulfonic (triflic) anhydride were used without further purification. 2-(Perfluorooctyl)ethyl alcohol (mp 40 °C) was supplied from Asahi Glass Co. and used without further purification. All distillations were carried out under nitrogen.

Preparation of *n*-Octyl Triflate (OcOTf).[9] To a slurry of 8.3 g (0.06 mol) of anhydrous potassium carbonate, 2.0 g (0.015 mol) of 1-octanol, and 10 mL of CH_2Cl_2 was added 5.3 g (0.019 mol) of triflic anhydride in 5 mL of CH_2Cl_2 at 0 °C over 1 h. The mixture was stirred at 0 °C for 7 h and filtered. The solvent was evaporated from the filtrate and the residue was distilled to give 2.2 g (56%) of OcOTf: bp 61–62 °C (0.8 mmHg); NMR ($CDCl_3$) δ 0.9 (t, J = 4 Hz, CH_3CH_2, 3 H), 1.3 (br, $CH_3(CH_2)_6CH_2$, 12 H), 4.5 (t, J = 6 Hz, CH_2O, 2 H).

Similarly, two other triflates were prepared. *n*-Dodecyl triflate (DoOTf): oil, NMR ($CDCl_3$) δ 0.9 (t, J = 4 Hz, CH_3CH_2, 3 H), 1.3 (br, $CH_3(CH_2)_{10}CH_2$, 20 H), 4.5 (t, J = 6 Hz, CH_2O, 2 H).

2-(Perfluorooctyl)ethyl triflate: white crystals, bp 62 °C (0.3 mmHg); NMR (CDCl$_3$) δ 2.7 (t of t, J = 6, 17 Hz, CF$_2$CH_2CH$_2$, 2 H) 4.8 (t, J = 6 Hz, CH_2O, 2 H).

Preparation of *n*-Octyl Tosylate (OcOTs).[10] To the solution of 4.6 g (0.024 mol) of tosyl chloride in 10 mL of pyridine, 2.9 g (0.022 mol) of *n*-octanol in 5 mL of pyridine was added dropwise at 0 °C. The mixture was stirred at 0 °C for 9 h and hydrolyzed with water. The mixture was taken up into diethyl ether, washed with water, and dried over MgSO$_4$. The solvents were evaporated in vacuo and the residue was distilled to give OcOTs: bp 135–137 °C (0.25 mmHg); NMR (CDCl$_3$) δ 0.9 (br, CH_3CH$_2$, 3 H), 1.2 (br, CH$_3$(CH_2)$_6$CH$_2$, 12 H) 2.5 (s, CH_3–Ar, 3 H), 4.1 (t, J = 6 Hz, CH_2O, 2 H), 7.4 and 7.8 (two d, J = 8 Hz, CH$_3$C$_6$H$_4$SO$_3$, 4 H).

Polymerization via a Fast Initiation Method. A typical run was as follows (entry 3). In a glass tube, 0.7 mmol of *n*-octyl triflate was dissolved in 2 mL of acetonitrile, and 4.0 mmol of MeOZO was added dropwise at 0 °C under nitrogen. The tube was sealed and kept at 80 °C for 18 h. The tube was opened and the reaction mixture was poured into 60 mL of diethyl ether to precipitate a polymeric material. After a reprecipitation procedure using acetonitrile as a solvent and diethyl ether as a nonsolvent, the polymeric material was collected and dried in vacuo to give 0.49 g (93% yield) of a white powdery material.

Preparation of α,ω-Dodecamethylene Bis(tosylate) (10).[11] In a 100-mL, two-necked flask were placed 4.05 g of 1,12-dodecanediol and 30 mL of pyridine. The flask was cooled in an ice bath and then 9.16 g of tosyl chloride was added. The content of the flask was stirred and cooled below 10 °C for 6 h. The pinkish precipitate was isolated by filtration and washed with 60 mL of aqueous HCl solution and 180 mL of ice water. The isolated white crystal was purified by reprecipitation (chloroform as a solvent and petroleum ether as a nonsolvent) twice to give 7.2 g (71% yield) of α,ω-dodecamethylene bis(tosylate) (**10**): ^{1}H NMR (CDCl$_3$) δ 1.2 (s, C(CH$_2$)$_{10}$C, 20 H), 2.5 (s, CH_3–Ar, 6 H), 4.1 (t, OCH$_2$C, 4 H), 7.4 and 7.9 (two d, CC$_6$H$_4$S, 8 H).

Polymerization for ABA-Type Block Copolymers. In a glass tube, 0.15 mmol of α,ω-dodecamethylene bis(tosylate) (**10**) was dissolved in 0.52 mL of acetonitrile, and 1.9 mmol of MeOZO was added at 0 °C under nitrogen. The tube was sealed and kept at 80 °C for 16 h. After the polymerization was completed, the reaction mixture was poured into 30 mL of diethyl ether to precipitate a polymeric material. After a reprecipitation procedure using acetonitrile as solvent and diethyl ether as nonsolvent, the polymeric material was collected and dried in vacuo to give 0.20 g of pale yellowish powdery materials of **11** (84% yield).

Preparation of *N*-Methyl-2-*n*-octyl-2-oxazolinium Tosylate (12b). In a glass tube, 6.6 mmol of OcOZO and 17.7 mmol of MeOTs were dissolved in 2.5 mL of diethyl ether under nitrogen. The tube was sealed and kept at 80 °C for 2 h. After the reaction was completed, the reaction mixture was poured into 50 mL of diethyl ether to precipitate white crystals. After filtration and washing with diethyl ether the crystal was further purified by reprecipitation (a solvent was acetonitrile and a nonsolvent was diethyl ether) twice to give 1.56 g (64% yield) of *N*-methyl-2-*n*-octyl-2-oxazolinium tosylate (**12b**): ^{1}H NMR (CD$_3$CN) δ 0.9 (s, CH$_3$C, 3 H), 1.2 (s, C(CH$_2$)$_6$C, 12 H), 2.3 (s, CH_3–Ar, 3 H), 2.6 (br, O===C(CH$_2$)===N, 2 H), 3.3 (s, NCH$_3$, 3 H) 4.3 (t, NCH_2CH$_2$O, 2 H), 4.9 (t, NCH$_2$CH_2O, 2 H), 7.2 and 7.7 (two d, CC$_6$H$_4$S, 4 H). Anal. Calcd for C$_{19}$H$_{31}$NO$_4$S: C, 61.76; H, 8.45; N, 3.79. Found: C, 61.80; H, 8.59; N, 3.67.

Similarly, ***N*-methyl-2-dodecyl-2-oxazolinium tosylate (12a)** was obtained from DoOZO and MeOTs in 45% yield: ^{1}H NMR (CD$_3$CN) δ 0.9 (s, CH$_3$C, 3 H), 1.3 (s, C(CH$_2$)$_{10}$C, 20 H), 2.4 (s, CH_3–Ar, 3 H), 2.6 (br, O===C(CH$_2$)===N, 2 H), 3.3 (s, NCH$_3$, 3 H), 4.2 (t, NCH_2CH$_2$O, 2 H), 4.8 (t, NCH$_2$CH_2O, 2 H), 7.2 and 7.8 (two d, CC$_6$H$_4$S, 4 H). Anal. Calcd for C$_{23}$H$_{39}$NO$_4$S: C, 64.91; H, 9.23; N, 3.29. Found: C, 64,64; H, 9.34; N, 3.29. ***N*-Methyl-2-pentyl-2-oxazolinium tosylate (12c)** was obtained from PeOZO and MeOTs in 68% yield. ^{1}H NMR (CD$_3$CN) δ 0.9 (s, CH$_3$C, 3 H), 1.3 (br, C(CH$_2$)$_3$C, 6 H), 2.3 (s, CH_3–Ar, 3 H), 2.6 (br, O===C(CH$_2$)===N, 2 H), 3.2 (s, NCH$_3$, 3 H), 4.2 (t, NCH_2CH$_2$O, 2 H), 4.8 (t, NCH$_2$CH_2O, 2 H), 7.2 and 7.7 (two d, CC$_6$H$_4$S, 4 H). Anal. Calcd for C$_{16}$H$_{25}$NO$_4$S: C, 58.69; H, 7.70; N, 4.28. Found: C, 57.91; N, 7.80; N, 4.18. ***N*-Methyl-2-butyl-2-oxazolinium tosylate (12d)** was obtained from BuOZO and MeOTs in 71% yield. ^{1}H NMR (CD$_3$CN) δ 0.9 (s, CH$_3$C, 3 H), 1.5 (br, C(CH$_2$)$_2$C, 4 H), 2.3 (s, CH$_3$–Ar, 3 H), 2.6 (br, O===C(CH$_2$)===N, 2 H), 3.2 (s, NCH$_3$, 3 H) 4.2 (t, NCH_2CH$_2$O, 2 H), 4.8 (t, NCH$_2$CH_2O, 2 H), 7.2 and 7.7 (two d, CC$_6$H$_4$S, 4 H). Anal. Calcd for C$_{15}$H$_{23}$NO$_4$S: C, 57.49; H, 7.40; N, 4.47. Found: C, 57.30; H, 7.56; N, 4.68. ***N*-Methyl-2-phenyl-2-oxazolinium tosylate (12e)** was obtained from PhOZO and MeOTs in 79% yield. ^{1}H NMR (CD$_3$CN) δ 2.3 (s, CH$_3$–Ar, 3 H), 3.4 (s, NCH$_3$, 3 H), 4.4 (t, NCH_2CH$_2$O, 2 H), 4.9 (t, NCH$_2$CH_2O, 2 H), 7.2–7.8 (br, CC$_6$H$_4$S and O===C(C$_6$H$_5$)===N, 9 H). Anal. Calcd for C$_{17}$H$_{19}$NO$_4$S: C, 61.24; H, 5.74; N, 4.20. Found: C, 60.84; H, 6.04; N, 4.31.

Polymerization Using Isolated Salt 12 as Initiator. A typical run was as follows (entry 39). In a glass tube, 0.40 mmol of *N*-methyl-2-*n*-octyl-2-oxazolinium tosylate (**12b**) was dissolved in 1.5 mL of acetonitrile, and 4.4 mmol of MeOZO was added at 0 °C under nitrogen. The tube was sealed and kept at 80 °C for 30 h. After the polymerization was completed, the tube was opened and the reaction mixture poured into 50 mL of diethyl ether to precipitate a polymeric material. After a reprecipitation procedure (acetonitrile–diethyl ether), the polymeric material was collected and dried in vacuo to give 0.52 g of a white powdery material of **13d** (96% yield). Anal. Calcd for C$_{60.6}$H$_{103.8}$N$_{11.4}$O$_{14.4}$S: C, 58.01; H, 8.34; N, 12.73; S, 2.56. Found: C, 57.73; H, 8.62; N, 12.63; S, 2.45.

Measurements. ^{1}H NMR spectra were recorded on a 60-MHz Hitachi R-20B NMR or 90-MHz Hitachi R-900 FT NMR spectrometer at 35 °C with Me$_4$Si standard. The molecular weight of polymers was measured by a Corona 117 vapor pressure osmometer in chloroform at 40 °C. Gel permeation chromatography (GPC) analysis was performed by using JASCO TRIROTOR with an RI detector under the following conditions: Shodex AC-803 column or JSP-101 column and chloroform eluent at a flow rate of 1.0 or 0.5 mL/min. The surface tension (γ) of aqueous polymer solutions (1.0 or 0.5 wt %) was measured by a Shimadzu Du Noüy tensiometer at an ambient temperature (15, 17, 19, 20, 29, or 31 °C). For an easier comparison, the γ values obtained at these temperatures were recalculated to the values at 20 °C according to the following temperature dependency of γ of water: $\gamma = \gamma_0 - 0.1416t - (2.5054 \times 10^{-4})t^2$ where γ_0 denotes the γ values at 0 °C and t is the temperature value in degrees Celcius.[12] This recalculation involves the assumption that the above relationship of water is applicable to the aqueous solutions containing 1.0 or 0.5 wt % of polymer.

Registry No. **2** (R$_1$ = Me), 38796-76-8; **2** (R$_1$ = C$_2$H$_5$), 69488-61-5; **2** (R$_1$ = C$_3$H$_7$), 25821-74-3; **4**, 32034-10-9; **10**, 36247-34-4; **12a**, 102976-67-0; **12b**, 102932-00-3; **12c**, 108665-76-5; **12d**, 102932-02-5; **12e**, 40743-19-9; MeOZO, 1120-64-5; MeOZO (homopolymer), 26375-28-0; EtOZO (homopolymer), 25805-17-8; PrOZO (homopolymer), 25822-74-6; MeOZI, 10431-93-3; MeOZI (homopolymer), 26284-00-4; OcOTs, 3386-35-4; DoOTs, 10157-76-3; C$_8$H$_{17}$OTf, 71091-89-9; MeOTf, 333-27-7; C$_{12}$H$_{25}$OTf, 75618-27-8; C$_8$H$_{17}$(CH$_2$)$_2$OTf, 53059-89-5.

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Synthesis and Properties of Poly(1-chloro-1-alkynes)

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ABSTRACT: 1-Chloro-1-hexyne, -1-octyne, and -1-decyne (ClC≡CR; R = n-C_4H_9, n-C_6H_{13}, and n-C_8H_{17}) polymerized with Mo catalysts [e.g., $MoCl_5$, $MoCl_5$—n-Bu_4Sn, and $Mo(CO)_6$—CCl_4—$h\nu$] in high yields to give new high molecular weight polymers ($\bar{M}_w$ ca. 2×10^5–2×10^6). 1-Chloro-1-hexadecyne, which has a long alkyl group (R = n-$C_{14}H_{29}$), polymerized similarly, whereas 1-chloro-3-propyl-1-hexyne, which has a *sec*-alkyl group [R = $CH(n$-$C_3H_7)_2$], hardly polymerized owing to the steric reason. The product polymers had the structure of $-(CCl{=}CR)_n-$ according to the spectroscopic analyses. The polymers of 1-chloro-1-hexyne, -1-octyne, and -1-decyne were white solids, while poly(1-chloro-1-hexadecyne) was a white rubbery material. They were totally soluble in many organic solvents, thermally fairly stable in air, amorphous, film-forming, electrically insulating, and nonparamagnetic.

Introduction

Polymers obtained from substituted acetylenes have alternating double bonds in the main chain and various groups in the side chain. Unlike the unsubstituted polyacetylene, many of them are stable to air and soluble in organic solvents. Catalysts based on groups 5 and 6 transition metals (Nb, Ta, Mo, and W) have been found effective in their synthesis.[2]

Many 1-halo-1-alkynes have been prepared so far.[3] The halogen atoms in 1-halo-1-alkynes are expected to have various effects such as inductive, mesomeric, and steric ones on the C≡C bond, which has incited many organic chemists to study their reactivity.[4] In general, 1-chloro-1-alkynes are more stable in air at high temperature than other 1-halo-1-alkynes and hence are easier to handle.

To date, several polymers of 1-halo-1-alkynes have been known:[5] ClC≡CPh, ClC≡C—n-C_6H_{13}, BrC≡CPh, and BrC≡$C(CH_2)_4Br$. 1-Chloro-2-phenylacetylene polymerizes with only Mo catalysts to give a totally soluble high molecular weight polymer (MW ~ 1×10^6).[5a,5b] A recent short communication by us has revealed that 1-chloro-1-octyne also yields a high molecular weight polymer.[5c] In contrast, the polymer molecular weights of 1-bromo-1-alkynes (BrC≡CPh[5d] and BrC≡$C(CH_2)_4Br$[5e]) are no more than 1×10^4. Thus, it seems of great interest to examine the polymeriztion of various aliphatic 1-chloro-1-alkynes in detail.

The present paper deals with the synthesis and properties of poly(1-chloro-1-alkynes). New, high molecular weight polymers have been successfully synthesized from linear 1-chloro-1-alkynes (1-chloro-1-hexyne, -1-octyne, -1-decyne, and -1-hexadecyne) and their structure and properties have been clarified.

Results and Discussion

Polymerization of 1-Chloro-1-hexyne, 1-Chloro-1-octyne, and 1-Chloro-1-decyne. Table I gives results on the polymerization of three alkynes with C_4–C_8 alkyl groups, especially 1-chloro-1-octyne, in the presence of various catalysts. 1-Chloro-1-octyne polymerized only with Mo catalysts and did not yield any polymer (methanol-insoluble product) with W, Nb, Ta, Fe, or Ti catalysts. Difficulty of this monomer to polymerize with W catalysts coincides with the general tendency of 1-halo-1-alkynes,[5] and it should be associated with the electron-withdrawing property of the chlorine atom. It is known that Nb and Ta catalysts work well even for the polymerization of sterically crowded acetylenes as 1-(trimethylsilyl)-1-propyne.[2a] Hence, the result that 1-chloro-1-octyne does not polymerize with Nb or Ta catalysts is attributable to the electronic effect of the monomer. There has been no example of disubstituted acetylenes polymerizable with Ziegler catalysts (e.g., Fe and Ti catalysts); the present result for 1-chloro-1-octyne is consonant with it.

1-Chloro-1-hexyne, -1-octyne, and -1-decyne polymerize even with $MoCl_5$ alone in high yields under the conditions shown in Table I. However, use of n-Bu_4Sn, which reduces and/or alkylates $MoCl_5$, as cocatalyst accelerates the polymerizations (see below) and enhances the $\bar{M}_w$'s of polymers close to 1×10^6. The catalyst obtained by UV irradiation of the CCl_4 solution of $Mo(CO)_6$ effects still higher $\bar{M}_w$'s around 2×10^6. Thus, the $Mo(CO)_6$–CCl_4–$h\nu$ catalyst is suitable to accomplish very high molecular weight (the $MoCl_5$–cocatalyst systems, however, surpass it with regard to their higher activity and the ease of their preparation).

Table II shows what organometallics are useful as cocatalysts. As seen in the polymerization of 1-chloro-1-octyne, organometallics containing groups 4 and 5 main-group metals (Sn, Si, Sb, and Bi) generally give high yields of polymers with high molecular weights. In contrast, with organolithiums and -aluminum were formed appreciable amounts of methanol-soluble oligomers. This can be atttributed to their rather too strong reducing and alkylating ability (this is commensurate with the fact that $MoCl_5$ is excessively reduced to precipitate partly in the presence of these cocatalysts). Further, no polymer formed at all with the use of i-Bu_2AlH or 9-BBN, both of which have a metal–H bond.

For 1-chloro-1-hexyne, -1-octyne, and -1-decyne, groups 4 and 5 organometallic cocatalysts gave clearly better results than those in the absence of any cocatalyst; that is, both the yield and $\bar{M}_w$ of polymers tended to increase (Table II). In the case of organosilicons, no cocatalyst effect was observed unless they had a Si–H bond (e.g.,

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