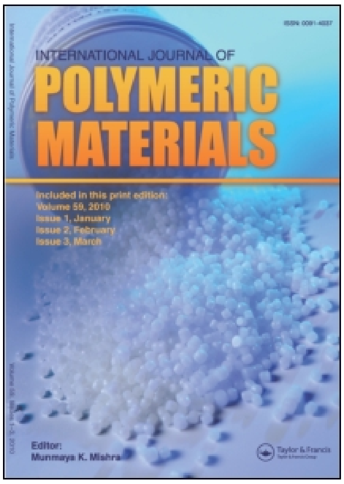

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IONIC POLYMERIZATION AND BLOCK AND GRAFT POLYMERS

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1. Introduction

A high degree of interest has been maintained in the fields covered by two of the sessions: "Ionic Polymerization" and "Block and Graft Polymerizations" which between them attracted 143 papers in total: cationic, 25; anionic, 36; coordination, 30; and block and graft, 52. The reviewer's impression is that the research in these areas is now more diversified than ever before, in particular the topics covered by the second session. The contributions focussed not only on the development of novel polymerization reactions, but also on their application to the synthesis of a wide variety of well-defined polymers. The following sections touch on some of the highlights; references are given in parentheses, where EA and ES refer to the pages of the *Polymer Preprints, Japan, English Edition* (Vol. 37) for the Annual Meeting (No.1) and the Symposium on Macromolecules (No.2), respectively.

2. Cationic Polymerization

Living Polymerization

In cationic polymerization, styrene derivatives are less reactive than vinyl ethers, and thus living polymerization of the aromatic alkenes has been difficult. Using an initiating system based on hydrogen iodide (HI), however, Higashimura and his co-workers have succeeded in the living cationic polymerizations of *p*-methoxy- and *p*-methylstyrenes. Monodisperse living polymers ($\bar{M}_w/\bar{M}_n < 1.1$) of the *p*-methoxy derivative were obtained at room temperature using HI/ZnI_2 as the initiating system for the polymerization in toluene (125, EA40; 1309, ES21). The corresponding reaction in CH_2Cl_2

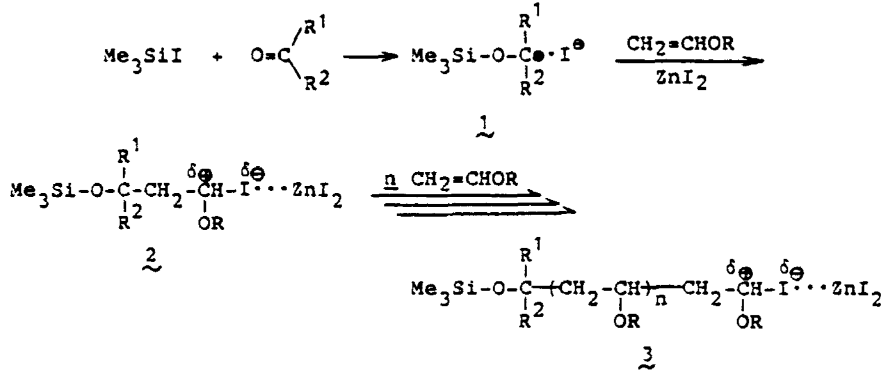
resulted in a mixture of living (lower MW) and nonliving (higher MW) polymers that showed a bimodal molecular weight distribution (MWD). Addition of tetra-*n*-butylammonium halides ($n\mathrm{Bu_4NX}$; X = I, Br, Cl) to the polar solvent eliminates the latter fraction and in turn leads to a truly living polymerization, again operable at room temperature.

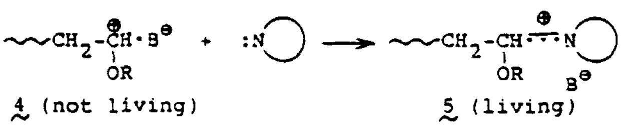
The best initiating system for the living cationic polymerization of *p*-methylstyrene turned out to be a combination of HI and excess $ZnCl_2$ (1309, ES21). The polymerization may be carried out in both toluene and CH_2Cl_2 (without $n\mathrm{Bu_4NX}$) below 0°C; the resultant living polymers have slightly broader MWDs ($\bar{M}_w/\bar{M}_n = 1.1–1.3$) than those for *p*-methoxystyrene.

Developments of new initiating systems for living vinyl ether polymerization were also reported by the same group from Kyoto University. One of them involves trimethylsilyl iodide (Me_3SiI) and ZnI_2 for the polymerization of isobutyl vinyl ether (IBVE) (124, EA40; 1318, ES24). Although apparently equivalent in function to HI, the silyl iodide needs a carbonyl compound (acetone, benzaldehyde, etc.) for quantitative initiation, with which it reacts to form the initial step to form a cation **1** (Scheme 1). The subsequent attack of **1** on IBVE yields an intermediate **2** that in turn grows into a living polymer **3** carrying an active site identical to that obtained with HI/ZnI_2. The living polymerization of IBVE by the Me_3SiI/ZnI_2/benzaldehyde system operates in toluene at room temperature or below. Acidolysis of the silyloxyl group of **3** leads to an alcoholic termial group.

The second example utilizes the $CH_3CH(i\mathrm{Bu})OCOCH_3/EtAlCl_2$ system in conjunction with a basic additive, including not only ethers (122, EA39) but an amine (2,6-dimethylpyridine) (1312, ES22) as well; the bases are

Scheme 1

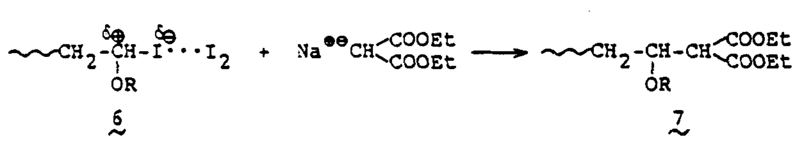




(1)

responsible for stabilizing the unstable growing carbocation **4** into a living form **5** (eq. 1). The former paper points out that the minimum amount of ethers required for a living process decreases with an increase in their basicity (ethyl ether >1,4-dioxane>THF). The latter reveals the importance of steric crowding around the amine's nitrogen; the use of less crowded amines (Et_3N and pyridine) in place of the 2,6-dimethyl analog results in termination irrespective of their basicity.

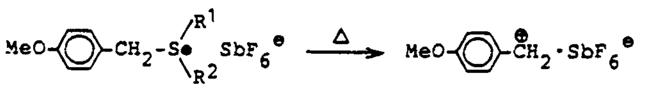
Higashimura's group also has determined the concentration and lifetime of the HI/I_2-initiated living poly(IBVE) **6** by quenching with sodiomalonic ester (eq. 2) (1315, ES23). The living end concentration, measured by ^1H-NMR analysis of the malonate terminal group of **7**, was found to decrease after complete consumption of the monomer. The lifetime, however, was relatively long and found to be of the order of hours in toluene.



(2)

Thermally Latent Catalysts

Endo *et al.* studied the cationic polymerization of styrene with sulfonium salts (eq. 3) that yield the initiating *p*-methoxybenzyl cation only above a certain temperature and hence are named thermally latent catalysts (116, EA36; 1324, ES26). The onset temperatures for the methoxy derivatives **8** (<50°C) are lower than those for the nonsubstituted form (>80°C) and depend on the substituents R^1 and R^2 in **8** [Et<Me<$(CH_2)_4$]; the order appears to correlate with the bulkiness of R^1 and R^2. The polymerization was carried out in bulk with 0.1 mol% catalyst to give polystyrene with $\bar{M}_n = 2000–12000$ in 24–78% yield depending upon the conditions used.



(3)

8 [R^1R^2 = Me, Et, $-(CH_2)_4-$]

Copolymerization of Benzene and Toluene

Under an atmosphere of oxygen, a mixture of $AlCl_3$ and CuCl (3/1 molar ratio) efficiently polymerizes benzene and toluene via oxidative coupling to form poly(*p*-phenylenes). Noting the insolubility of these polymers, Toshima employed his $AlCl_3/CuCl/O_2$ catalyst for the copolymerization of the two monomers (139, E47). The catalyst works well at 50°C, giving partially methylated polyphenylene in 290% yield (based on CuCl) in 24 hr from an equimolar monomer mixture. The product consists of benzene soluble and insoluble parts, both of which prove to be true copolymers. In contrast to homopoly(*p*-phenylene), the latter is completely soluble in chloroform.

3. Anionic Polymerization

Living Polymerization using Aluminum Porphyrin

The scope of the living polymerization with aluminum porphyrin complexes (eg. **9**) has been extended from heterocycles and methyl methacrylate (MMA) to acrylates and nitriles (99–101, EA27–28; 1327, ES27). For example, the methyl analog **9a** permits a visible light induced living polymerization of methyl methacrylate (MMA) for which aluminum enolate **9c** is proposed as the growing species (1330, ES28); irradiation is indispensable for the initiation process. Inoue and Aida (99, EA27), however, found that the thiolate porphyrin **8b** mediates a similar living process in the dark to yield monodisperse polymers with 100% initiation efficiency (Table 1, entry 1 and 2).

TABLE I
Living Polymerization by Aluminium Porphyrin 9 in CH_2Cl_2*

Monomer	Initiator	Temp, °C	M_n	M_w/M_n	Entry
$CH_2=C^{Me}_{COOMe}$	9b(R = *n*Pr)	+35	22,000	1.12	(1)
	9b (R = Ph)	+80	15,000	1.18	(2)
$CH_2=C^{H}_{COOtBu}$	9b(R = *n*Pr)	−70	10,000	1.14	(3)
	9c (n = 100)	+35	22,400	1.12	(4)
$CH_2=C^{H}_{COOEt}$	9c	−70	—	1.25–1.43	(5)
$CH_2=C^{Me}_{CN}$	9c(n = 40)/ light/pyridine	+35	7,640	1.26	(6)

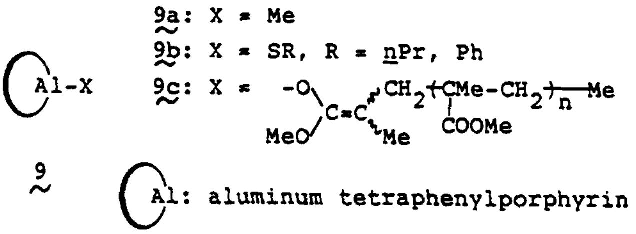
* References: entry 1 and 2 (99, EA27); entry 3–5 (100, EA28); entry 6 (101, EA28). See also (1327, ES27).

TABLE II
Living Anionic Polymerization of Functionalized Styrenes $CH_2=CH-C_6H_4-X(p)$: [in THF at −78°C; counterion, K(average)(Li(average) for 14)]

X	$-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{CH}}}$	$-CH_2\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{CH}}}$	$-SO_2NEt_2$	$-SO_3Et$
Code	10	11	12	13
$M_n/(M_w/M_n)$	14000/1.14	20000/1.09	12000/1.17	5100/1.10
Ref.	(104, EA30)	(104, EA30)	(106, EA31)	(1339, ES31)
X	$-N(SiMe_3)_2$	$-NMe_3$	$-CH_2NMe_2$	$-CH_2CH_2NMe_2$
Code	14	15	16	17
$M_n/(M_w/M_n)$	43000/1.08	27000/1.05	35000/1.09	30000/1.08
Ref.	(112, EA34)	(1351, ES35)	(1351, ES35)	(1351, ES35)

The thiolate **9b** and polymeric enolate **9c** are also effective in living polymerization of acrylates (Table 1, entry 3–5) (100, EA28). The latter appears better in order to keep the reaction homogeneous and gives MMA-acrylate block polymers. Probably because of the acidic protons of the monomers, the polymerization temperature for ethyl and isobutyl acrylates should be lowered to −70°C.

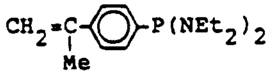
Inoue's reaction with **9c** is shown to operate also for methacrylonitrile, but in this case visible light irradiation and the presence of pyridine as a base are needed (Table 1, entry 6) (101, EA28). The effect of irradiation upon the polymerization rate is more remarkable for methacrylonitrile than for MMA for which pyridine does not accelerate but retards the reaction. Another interesting finding is that the MMA polymerization by **9a** can be greatly accelerated by organoaluminums ($AlMe_3$, $AlEt_3$, and Et_2AlCl); polymer molecular weight, however, is still determined by the MMA/**9a** feed ratio (102, EA29; 1330, ES28).



Living Polymerization of Functionalized Styrenes

There is a continuing expansion of the list of functionalized styrenes that can be polymerized anionically into living polymers. Table 2 presents examples reported by two groups led by Nakahama (**10–13**) and by Fujimoto (**14–17**). The polymerizations were carried out at –78°C in THF where the potassium cation was found to be the best counterion for most of the monomers. For the polymerizations of **12**, **13**, and related styrenic monomers, Nakahama concluded, as expected, the electron withdrawing substituents decrease the nucleophilicity of the growing carbanions and thereby render them less reactive (1339, ES31).

The rigorous experiments by Fujimoto and Se established the best reaction conditions for **15–17** (1351, Es35). The amino groups of the polymers of **16** and **17** can readily be quarternized with *n*-butyl bromide to give a water-soluble polymer. Upon treatment with *p,p'*-bis(chloromethyl)azobenzene, the same polymers form crosslinked films that undergo uv-induced cis-trans isomerization of the azobenzene units. Another report by the same group describes the living polymerization of a phosphorus-containing monomer **18** with *n*BuLi ($\bar{M}_n = 62000$, $\bar{M}_w/\bar{M}_n = 1.09$) (1354, ES36).


18

Stereochemical Control

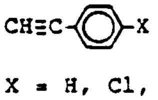
An initiating system consisting of *t*-butyl lithium and an alkyl aluminum (*t*BuLi/AlR$_3$; R = Me, Et, *n*Bu, *i*Bu, *n*Oct; Al/Li $\geq$ 3) was found to allow living polymerizations of MMA and related methacrylates in toluene below −78°C, where highly syndiotactic polymers result [$S(rr \geq 90\%$; $\bar{M}_w/\bar{M}_n$-1.1–1.2] (110, EA33; 1306, ES20). The best run for MMA was carried out at −93°C with Al(*n*Oct)$_3$ to give 96% syndiotacticity ($M_n = 3820$, $\bar{M}_w/\bar{M}_n = 1.18$). The *t*BuLi/AlR$_3$ system adds the third entry to Hatada's initiators for stereoregular anionic polymerization, following *t*BuMgBr (isotactic) and AlEt$_3$/PR$_3$ (syndiotactic).

4. Coordination Polymerization

Stereoregular Polymerization of Acetylenes

With use of rhodium complexes in ethanol at 30°C, Tabata and Sohma prepared perfectly cis-transoidal polymers from *p*-substituted phenylacetylenes (**19**) (147, EA51; 1266, ES4). The near 100% cis selectivity was achieved by using (1,5-cyclooctadiene)$_2$Rh$_2$Cl$_2$ and (norbornene)$_2$Rh$_2$Cl$_2$ for X = OMe and H; the $\bar{M}_w$ of the polymers ranged $(10\text{—}26) \times 10^4$. The polymerization of the chloro derivative with the latter complex can be carried out on a glass plate to give a tough, semitransparent, dark yellow film that turns opaque and orange on treatment with hot benzene or toluene. The two rhodium complexes and their derivatives are also effective in polymerizing 2-pyridilacetylene (**20**) into a perfectly cis polymer in 40–65% yield (1269, ES5).

The researchers of Hokkaido University have also observed by ESR and ^{1}H NMR (sharp singlet at 5.85 ppm) that the cis polymers (**19**) undergo thermal cis-trans isomerization at 120°C where the radical concentration sharply increases by factor of 200 (148, EA52; ES4). They attributed these findings to the formation of at least two solitons (radicals stabilized by a conjugating system).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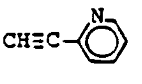
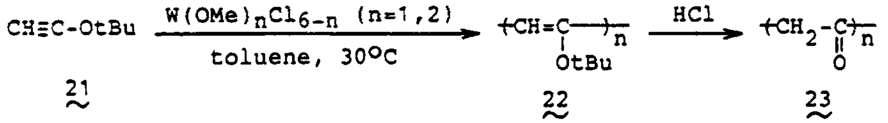
(X = H, Cl, OMe)


20

Poly (β-ketones) from Alkoxyacetylenes

t-Butylacetylene was polymerized by Kobayashi using $W(OMe)_4Cl_3$ or $W(OMe)_5Cl$ as initiator in toluene at 30°C (Scheme 2) (1363, ES39). The polymers (MW = 2500, yield = 18–19%) proved to have the expected linear structure **22** and can be converted into a poly(*β*-ketone) **23** by treating with hydrochloric acid. The polymerizations with stronger tungsten salts (WCl_6 and WCl_6/Ph_4Sn) are accompanied by isomerization of repeat units.

Scheme 2



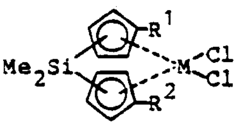
Living Polymerization

Masuda and Higashimura studied in detail the living polymerization of 1-chloro-1-hexyne ($ClC{\equiv}C\text{-}n\text{-}C_6H_{13}$) by the $MoOCl_4/n Bu_4Sn/EtOH$ initiating system (146, EA51); $\bar{M}_n$ = (5–13 × 10^4 $\bar{M}_w/\bar{M}_n$ = 1.16–1.23, initiation efficiency = 3–7%/Mo). The ethanol in the initiating system may be replaced with other oxygen-containing compounds such as ethyl acetate and related esters and alcohols.

A homogeneous binary initiator, $V(acac)_3/Et_2AlCl$, was applied to copolymerization of propylene with nonconjugated diolefins (e.g., 1,4-hexadiene and 1,7-octadiene) by Doi and Soga, who obtained living copolymers with $\bar{M}_w/\bar{M}_n = 1.3$ and $\bar{M}_n < 20000$ (132, EA44). The products exhibited slightly broader MWDs than the corresponding homopolypropylene and may involve isomerized repeat units of the diolefins.

New Catalysts for Olefin Polymerization

For propylene polymerization, two series of new coordination catalysts based on Zr or Hf were independently developed by research groups of Chisso Petrochemicals and Idemitsu Kosan, Chisso's series consists of methylaluminoxane (MW = 700–1000) and metal complex **24** carrying two silicon-bridged cyclopentadiene



24
M = Zr, Hf
R^1, R^2 = H, Me, tBu

ligands (1285, ES13). Among various combinations of the central metal and ligand substituents, the catalyst with M = Zr and R^1 = R^2 = Me (Al/Zr = 10^4 molar ratio) most effectively polymerizes propylene in toluene at 30°C to yield isotactic polymers (*mm–mm* = 92.5%; $\bar{M}_w$ = 9400, $\bar{M}_w/\bar{M}_n$ = 2.38; mp = 146.2°C; 144 kgPP/g-metal.hr). The Hf derivative of **24** leads to higher polymer molecular weights but lower catalyst activity.

The second example (134, EA45; 135, EA45) also utilizes methylaluminoxane in conjunction with Cp_2MCl_2 (Cp = cyclopentadienyl, 1,2,3,4,5-pentamethyl-cyclopentadienyl; M = Ti,Zr, Hf); the catalysts are primarily for the synthesis of propylene oligomers with vinyl terminals. The objective was achieved with use of the methyl-substituted Cp ligands that led to low oligomers ($\bar{M}_n$ = 150–220; dimers-tetramers) in which the terminal vinyl content reached 92–98%.

5. Graft and Block Polymers

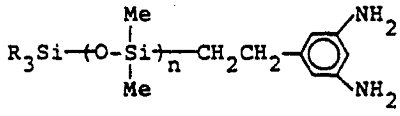
Macromonomers and Graft Polymers

A variety of macromonomers (18 papers in total) were reported this year, and the representative examples are shown as **25–30**. High interest was also focused on siloxane polymers (9 papers) as components of macromonomers and block polymers. A group from the Sagami Chemical Research Center prepared a polysiloxane macromonomer **25** with a diamine terminal (167, EA61). Condensation polymerization of **25** with pyromellitic dianhydride and *m*-phenylenediamine gives a polyimide (backbone)/polydimethylsiloxane (branch) graft polymer. The imide/siloxane graft is stable up to 280°C (slightly inferior to polyimide) and showed selectivity for organic liquids over water (opposite to polyimide).

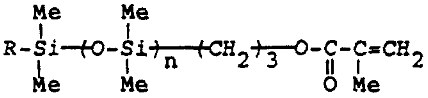
Heterotelechelic polysiloxane macromonomers **26** were obtained by Suzuki and Okawa of Toray Silicon (169, EA62). The methacrylate end of **26** ($\bar{M}_n$ = 6100) was first allowed to copolymerize radically with styrene or MMA into graft polymers [$\bar{M}_w$ = (2–7) × 10^4]. The pendant silylalkenyl functions were subsequently treated with $(Me_2HSiO)_4Si$ in the presence of a Pt catalyst to give insoluble crosslinked materials [polystyrene- or poly(MMA)-polysiloxane networks].

Imai and Tezuka copolymerized vinyl acetate with silyl-vinyl-capped macromonomers **27** (173, EA64) or **28** (174, EA65). Subsequent hydrolysis led to poly(vinylalcohol) (backbone)/polyether or polyamine (branch) graft polymers (1463, ES72). The macromonomer synthesis was based on living polymerization of THF (for **27**) and *t*-butylaziridine (for **28**).

Another examaple of macromonomers via a ring-opening polymerization is **29** ($\bar{M}_n$ = 580–2180) reported by Kobayashi *et al.* (166, EA61; 1472, ES75), among which the water-soluble version (**29**, R = Me) from

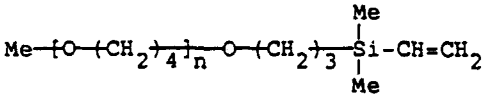


25
R = Me, $CH_2CH_2C_6F_{13}$
n = 4 - 20



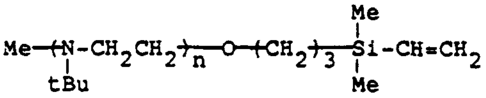
$R-Si(Me)_2-(O-Si(Me)_2)_n-(CH_2)_3-O-C(=O)-C(Me)=CH_2$

26
R = vinyl, allyl, hexenyl



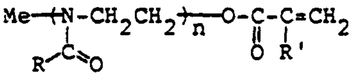
$Me-(O-(CH_2)_4)_n-O-(CH_2)_3-Si(Me)_2-CH=CH_2$

27

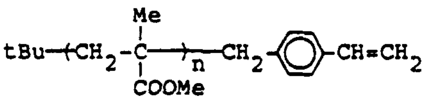


$Me-(N(tBu)-CH_2CH_2)_n-O-(CH_2)_3-Si(Me)_2-CH=CH_2$

28



29
R = Me, Et, nBu
R' = Me, H



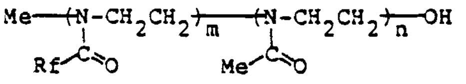
30

2-methyloxazoline is particularly interesting. For example, its radical copolymerization with styrene or MMA gives amphiphilic graft polymers that increase the wetability of glass and form micelles in D_2O or inverse micelles in C_6D_6.

Styrene-capped poly(MMA) macromonomers **30** with chemically identical but stereochemically opposite backbones were prepared by living anionic polymerization of MMA; the initiators of choice were *t*BuMgBr/HMPA for the isotactic backbone (*mm* = 90%) and *t*Buli/AlEt$_3$ for the syndiotactic backbone (*rr* = 88%) (165, EA60; 1487, ES80). Hatada *et al.* compared the radical polymerization rates of these polymeric styrenes ($\bar{M}_n$ = *ca* 3000); the isotactic isomer is slightly more reactive.

Block Polymers

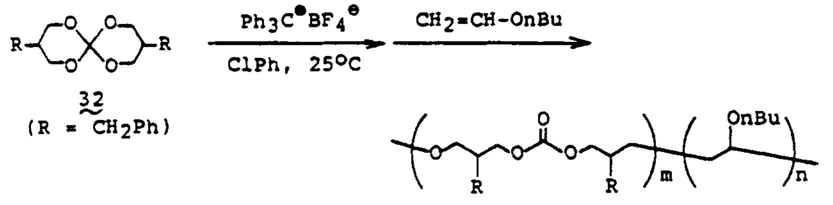
The research group led by Saegusa applied their living polymerization of 2-oxazolines to the synthesis of amphiphilic AB block polymers **31** with perfluoroalkyl pendant groups. One series (R_f = *n*-C_3F_7, *m* = 2.8 *n* = *4–8)*; $\bar{M}_n$ = *1000-1350)* was found to be effective in surface modification of poly(vinyl chloride) and nylon-6 (177, EA66), whereas another series exhibited excellent surface activity (1499, ES84). For example, the surface tension of water was reduced to 20–30 dyn/cm (cmc ≤ 10^{-2} wt%) by **31** with $R_f = C_2F_5$ or n-C_3F_7, m = 2–5, n = 5–11 and to 14–15 dyn/cm [cm = (4.8–7.2) × 10^{-3} wt%] with R_f = n-C_7F_{15}, m = 1, n = 1–3. The last version of **31** is perhaps the most active among the ionic and nonionic polymeric surfactants ever reported.



$Me\text{—}(N(COR_f)\text{-}CH_2CH_2)_m\text{—}(N(COMe)\text{-}CH_2CH_2)_n\text{—}OH$

31

$Rf = C_2F_5,\ nC_3F_7,\ nC_7F_{15}$



32

(R = CH_2Ph)

(4)

33

Endo *et al.* found that the cationic polymerization of spiroorthocarbonate **32** with Ph_3C BF_4 involves a long-lived intermediate from which n-butyl vinyl ether can be polymerized (eq 4.) The product **33** is a block polymer-consisting of ether carbonate and vinyl ether segments ($\bar{M}_n$ = 4500–5300, $\bar{M}_w/\bar{M}_n$ = 1.8–1.9).