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Oligomers Derived from 2-Oxazolines

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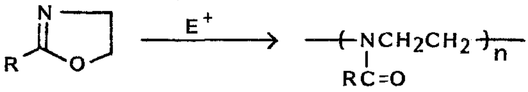
ABSTRACT

This paper describes the synthesis and properties of oligomer chains derived from 2-oxazolines. First, poly(styrene-*g*-*N*-acetylethylenimine) was prepared, and its hydrolysis gave poly(styrene-*g*-ethylenimine) which showed good chelating properties. Secondly, ABA type triblock copolymers were prepared in which an *N*-acylethylenimine chain is used as A block and ethylene oxide chain is employed as B block. These triblock copolymers showed good compatibility with Nylon 6, which were shown to posecess effective anti-electrostatic properties for Nylon 6. Thirdly, AB type block copolymers from 2-oxazolines have been prepared by using living polymerization technique. These block copolymers are soluble in water and showed good surfactant nature as reflected by surface tension (γ), when A block is consisted from *N*-acetyl- or *N*-propionylethylenimine chain (hydrophilic) and B block is made of *N*-tridecanoyl or *N*-aroylethylenimine chain (lipophilic). Finally, graft copolymers of cellulose diacetate having *N*-acetylethylenimine chain were prepared. It has been found by using a rheovibron that these graft copolymers are compatible with poly(vinyl chloride).

Cationic ring-opening polymerization of 2-substituted 2-oxazolines 1 is a versatile method to produce poly(*N*-acylethylenimine)s 2 [1-3].



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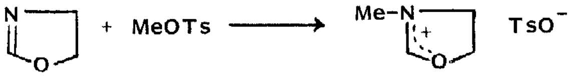
The mechanism of the polymerization has extensively been investigated from the kinetic viewpoint by using ^{1}H NMR spectroscopy. It has been established that there are two different propagating species; oxazolinium ion type and covalent type. The nature of the propagating species depends mainly upon the counter anion derived from the initiator and the monomer (the substituent at the C-2 position). The polymerization mechanism of unsubstituted 2-oxazoline 3 is given as a typical example [4]. With methyl tosylate (MeOTs) initiator, 3 proceeded via oxazolinium species (4-6), i.e.,

Initiation



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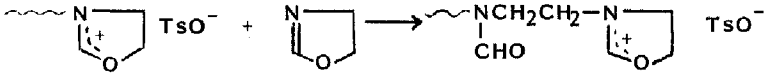
Propagation



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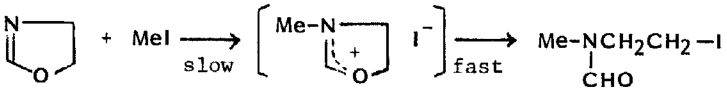
On the other hand, the polymerization with methyl iodide initiator occured via covalent propagating species of alkyl iodide type (8, 9, and 11), i.e.,

Initiation



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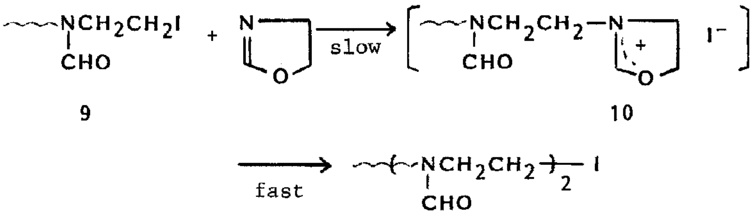
Propagation



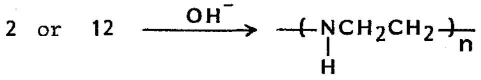
9 10

11

The type of the above propagating species are determined by the relative nucleophilic reactivities of the monomer and of the counter anion. Iodide anion is much more nucleophilic than **3**, and hence, an oxazoliniums of **7** and **10** are converted quickly into the corresponding covalent species of **8** and **11** before **7** and **10** are attacked by monomer **3**. Tosylate anion is less nucleophilic than **3**, and hence, **4**-**6** are stable propagating species.

The polymerization of 2-methyl-2-oxazoline was induced by MeOTs, methyl iodide, benzyl bromide, or benzyl chloride [5]. Among them, the benzyl chloride initiated system proceeded via alkyl chloride propagating ends whereas others via oxazolinium type propagating species in acetonitrile solvent.

The product polymers, **2** and poly(*N*-formylethylenimine) **12** from **3**, were hydrolyzed to give polyethylenimine **13** having a clear-cut linear structure [6].



$$2 \text{ or } 12 \xrightarrow{OH^-} \left(\underset{H}{\underset{|}{N}}CH_2CH_2 \right)_n$$

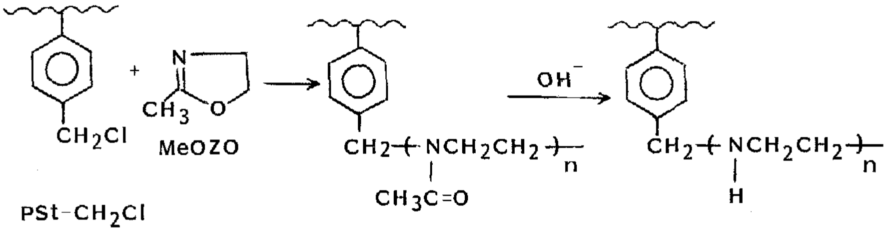
13

Thus, it has been shown that alkyl tosylates or halides induce the cationic polymerization of 2-oxazolines. On the basis of these findings several graft and block copolymers having oligomeric chains of *N*-acylethylenimine or ethylenimine unit have been prepared, which showed interesting and useful properties.

RESULTS AND DISCUSSION

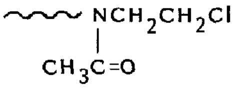
1. Poly(styrene-*g*-ethylenimine) for Chelating Resin

By utilizing the results that benzyl chloride induced the polymerization of 2-methyl-2-oxazoline(MeOZO), the chloromethylated polystyrene(PSt-CH_2Cl)(non-crosslinked or crosslinked) was used to initiate the MeOZO polymerization. Thus, poly(styrene-*g*-MeOZO) **14** was obtained, which was then subjected to alkaline hydrolysis to produce poly(styrene-*g*-ethylenimine) **15** [7].



14 15

During the graft copolymerization the addition of KI increased the total conversion of MeOZO as well as the grafted part(Figure 1). This effect is due to the exchange of the counter anion of Cl^- with I^-. The MeOZO polymerization by PSt-CH_2Cl proceeds via the alkyl chloride type propagating species **16** whereas that by MeI propagates via the oxazolinium species **17** in acetonitrile.



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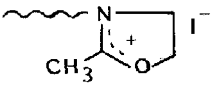

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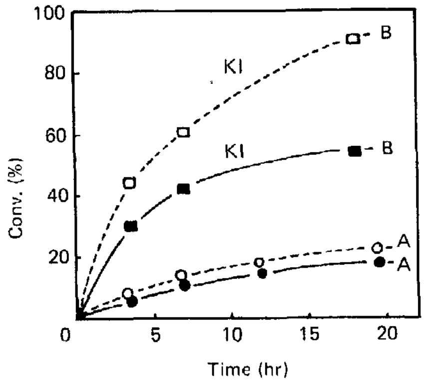


FIG.1 Effect of KI addition on the graft polymerization at 50°: (A) PSt-CH_2Cl(0.084 g) and MeOZO(0.60 ml) in 1.6 ml of DMF; (B) KI(0.11 g) was added to the system A; (○,□) total conversion of MeOZO; (●,■) grafted part.

The graft copolymer **15** having ethylenimine chain showed good chelating properties toward heavy metal ions such as Cu^{2+}, Cd^{2+}, and Hg^{2+} (Figure 2)[7]. It should be noted that the copolymer sample C-5H exhibited a greater adsorption capacity for Cu^{2+} than that of the commercial resin. It is also important to note that a resin like **15** is difficult to prepare by polymerizing ethylenimine with $PSt-CH_2Cl$ or by reacting a commercial branched polyethylenimine with $PSt-CH_2Cl$ [7].

2. Block Copolymer for Anti-electrostatic Agent

Block copolymers consisting of poly(*N*-acylethylenimine) and poly(ethylene oxide)(PEO) chains have been propared as an anti-electrostatic agent [8]. The preparation procedures are shown as follows. First, PEO glycol was converted to an α,ω-di-tosylated

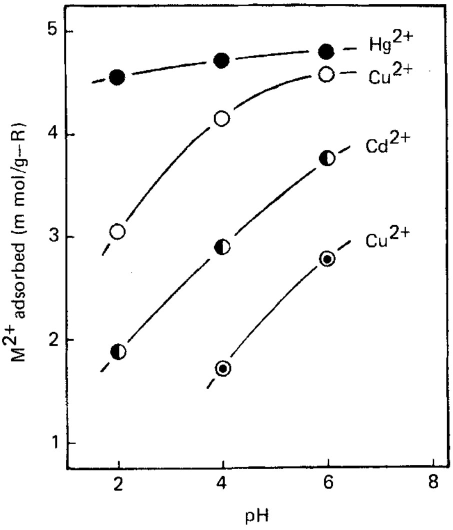
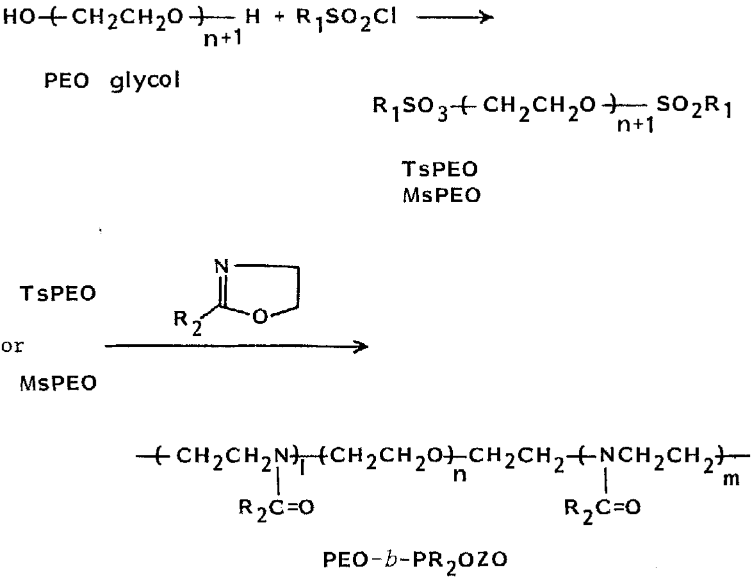


FIG. 2 Effect of pH on the adsorption of Cu^{2+}, Hg^{2+}, Cd^{2+} (30°C for 72 hr): (● ○ ◐) copolymer C-5H (0.25 g) in 50 ml of metal ion (0.025 mol/l.) solution; (◉) commercial resin (0.25 g) in 50 ml of Cu^{2+} (0.025 mol/l.) solution. Copolymer C-5H contains ethylenimine unit in 15.25 mmol/g and the degree of hydrolysis is 87.7%.

(TsPEO) or α,ω-di-mesylated form(MsPEO). Then, TsPEO or MsPEO was used to initiate the polymerization of MeOZO or 2-ethyl-2-oxazoline (EtOZO).



A typical example of the copolymerization is as follows. A mixture of EtOZO (20 mmol, 0.198 mol) and MsPEO (4.84 g, 3.0 mmol, MW of PEO chain = 1,400) in 60 ml of acetonitrile was kept at 100°C for 20 hr under nitrogen. The mixture was then poured into 3.5 l of diethyl ether to precipitate the copolymer, A pale yellow solid was obtained in 96% yield (23.62 g).

Data of molecular weight of block copolymers as well as PEO chains are summarized in Table 1. The formation of ABA type block copolymers was established by GPC analysis and the molecular weights determination. ^{1}H NMR analysis showed that a small fraction of the mesylate end group remained unreacted under some polymerization conditions. This implies that AB type block copolymer is included in the final product. The production of copolymers of this type was also supported by the results of kinetic analysis which indi-

TABLE 1. Data of Molecular Weight

No	Copolymer	PEO Chain[a]	by VPO[a]	by NMR[b]
1	PEO-*b*-PMeOZO	(1,990)	5,900	8,270
2	PEO-*b*-PMeOZO	(1,990)	4,040	5,430
3	PEO-*b*-PMeOZO	(2,780)	14,700	13,900
4	PEO-*b*-PEtOZO	(630)	4,000	4,260
5	PEO-*b*-PEtOZO	(1,050)	5,900	5,960
6	PEO-*b*-PEtOZO	(1,400)	10,700	9,500
7	PEO-*b*-PEtOZO	(1,990)	8,800	11,500
8	PEO-*b*-PEtOZO	(1,990)	5,600	7,230
9	PEO-*b*-PEtOZO	(2,780)	12,400	18,800

a Determined by VPO in $CHCl_3$ at 35°.
b Determined by integral ratio of the peaks in the ^1H NMR spectra.

cated the slow initiation with MsPEO ($k_i = 2.5 \times 10^{-5}$ 1/mol·sec in CD_3CN at 80°C) followed by the fast propagation ($k_p = 2.1 \times 10^{-3}$ 1/mol·sec in CD_3CN at 80°C).

PEO derivatives are often used as anti-electrostatic agent. Furthermore, poly(*N*-acetylethylenimine) and poly(*N*-propionylethylenimine) possess high compatibility with some of widely used polymers such as Nylon 6 and vinyl chloride-acrylonitrile copolymer. Poly(*N*-acylethylenimine) may be regarded as a polymer homologue of DMF or *N*,*N*-dimethylacetamide(DMAc). So, it is significant to compare the high compatibility of poly(*N*-acylethylenimine) with the misible nature of DMF or DMAc toward common organic solvents.

The spinning of a mixture of Nylon 6 and the copolymer (3 wt %) was carried out. It was expected that the PEO block in the copolymer increases the anti-electrostatic property poly(*N*-acylethylenimine) block in the copolymer which gives the compatibility for Nylon 6. The half-life time($t\frac{1}{2}$) of the decay of the electrical charge on the sample thread was measured as an index of the anti-electrostatic property. The shorter half-life time($t\frac{1}{2}$) indicates the better anti-electrostatic property of the block copolymer (Table 2). The poly(*N*-acylethylenimine) homopolymer (PMeOZO or PEtOZO) also showed moderate anti-electrostatic property, alshough the property reflect-

TABLE 2. Antistatic Property of Block Copolymers[a] under 60% Relative Humidity at 20°C

No[b]	(OZO/EO)[c] Unit ratio	$t_{1/2}$ (sec)
Control[d]		70
PMeOZO		3.4
1	1.43	1.2
2	0.74	0.6
3	1.79	1.0
PEtOZO		7.2
4	2.22	4.0
5	1.79	2.5
6	2.44	2.5
7	2.33	3.8
8	1.18	1.3
9	2.22	3.4

[a] Nylon 6 samples containing 3 wt % of the polymer.

[b] Numbers of sample polymers are the same as those of Table 1.

[c] Ratios of *N*-acylethylenimine unit to ethylene oxide unit in the block copolymers; Determined by the integral ratios in the ^{1}H NMR spectra.

[d] Pure Nylon 6 sample was used as a blank test.

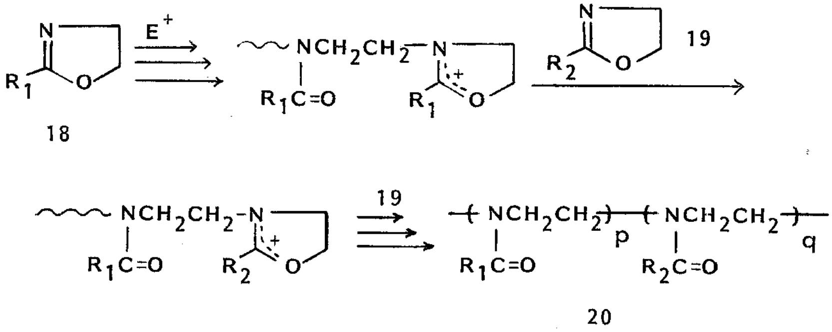
ed by $t_{1/2}$ was much less effective with the homopolymer than with the block copolymers. And, as the content of the PEO block in the copolymers increased, the anti-electrostatic property of the copolymer became better.

It is to be mentioned that the blend spinning of Nylon 6 could not be performed with the use of PEO or the mixture of PEO and PEtOZO because of the low compatibility of PEO with Nylon 6. Thus, the blend spinning of Nylon 6 and good anti-electrostatic properties for Nylon 6 are specific functions of these block copolymers.

3. Block Copolymers of 2-Oxazolines as a Non-ionic Polymeric Surfactant

The cationic ring-opening polymerizations of 2-oxazoline and some of its derivatives have been shown to proceed via living polymerization mechanism [1-3]. Therefore, it is easy to accomplish the so-called "one-pot two-stage copolymerization"; i.e., one of 2-

oxazoline monomer **18** such as MeOZO was first polymerized with MeOTs (1st stage polymerization), and then, the second monomer **19** such as 2-phenyl-2-oxazoline(PhOZO) was polymerized by the living propagating species of **18** (2nd stage polymerization)[9].



The product block copolymer **20** contains two different poly(*N*-acylethylenimine) segments within the same molecule. Results of the block copolymerization are shown in Table 3. The formation of block copolymers **20** is clearly shown by GPC analysis (Figure 3); Four sample polymers **20** (No 1-0——1-3) showed a single GPC peak, and hence, no homopolymer of MeOZO or PhOZO is contained in these copolymers. These results indicate that both stages of polymerization contain no chain-transfer and gave AB type copolymer quantitatively.

Poly(*N*-acetylethylenimine) having acetyl or propionyl group is hydrophilic, whereas that having a higher aliphatic acyl group or aroyl group is lipophilic. Thus, all block copolymers of **20** in Table 3 possess both hydrophilic and lipophilic blocks, and hence, are expected to exhibit surfactant properties. As an indication of surfactant nature the surface tension (γ) is measured in water in which all copolymers are soluble (Table 3). Among the copolymer samples the copolymer (No 5-1) from MeOZO and 2-lauryl-2-oxazoline (LaOZO) showed the best surfactant properties as reflected by γ value. It is to be noted that the critical micelle concentration (cmc) was less than 0.2 wt %. In addition, these block copolymers are non-toxic as shown by $LD_{50} > 2.0$ g/kg(mice) [9].

TABLE 3. Block Copolymers from 2-Oxazolines[a]

No	1st stage	2nd stage	Block Copolymers 20		
	1st monomer / Initiator molar ratio (°C, hr)	2nd monomer / Intiator molar ratio (°C, hr)	Mol. wt. (by VPO)	1st monomer / 2nd monomer unit value (p : q)	γ^b (dynes/cm)
	MeOZO	PhOZO			
1-0	5.2 (80, 15)	0	720	6.3 : 0	70.8
1-1	5.2 (80, 15)	5.2 (100, 18)	1630	6.3 : 6.2	52.1
1-2	5.2 (80, 15)	10.1 (100, 18)	2420	6.3 :11.6	52.5
1-3	5.2 (80, 15)	14.8 (100, 18)	2890	6.3 :14.8	54.6
3-0	15.4 (80, 15)	0	1720	18.0 : 0	70.0
3-1	15.4 (80, 15)	4.9 (100, 16)	2350	18.0 : 4.3	48.9
3-2	15.4 (80, 15)	10.4 (100, 16)	3040	18.0 : 9.0	51.2
	MeOZO	LaOZO			
5-1	5.2 (80, 15)	4.4 (100, 46)	1730	6.3 : 4.2	37.4
5-2	15.4 (80, 15)	5.1 (100, 46)	2700	18.0 : 4.1	46.6
	EtOZO	PhOZO			
6-1	10.4 (80, 15)	5.0 (100, 18)	2040	11.5 : 4.8	51.0
6-2	10.4 (80, 15)	9.9 (100, 18)	2930	11.5 : 9.5	49.5

[a] MeOTs initiator in CH_3CN. Copolymer yields were almost quantitative (>97%) in all cases.

[b] The surface tension was measured with a Du Noüy tensiometer with the polymer concentration =1.0 wt %, which is higher than cmc, at 29°C (γ of water at 29°C = 71.8 dynes/cm).

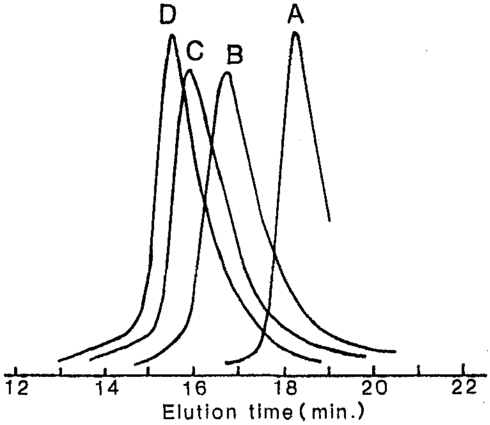


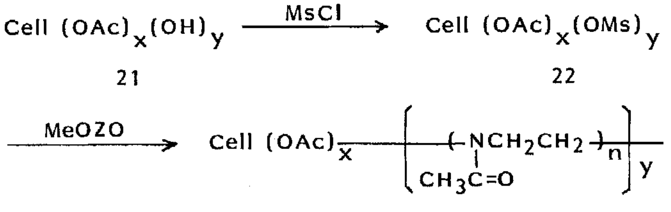
FIG. 3 GPC charts of four copolymers: A; Nol-0, B; Nol-1, C; Nol-2, D; Nol-3: eluent; $CHCl_3$, flow rate; 1.0 ml/min, column; Shodex A803, RI detector.

In relevant to block copolymers 20, a similar type of block copolymers consisting of poly(*N*-propionylethylenimine) and poly(*N*-lauroylethylenimine) has been prepared, and their surface tension was measured in chloroform, ethylene glycol, or methanol/water (80/20 in volume) by Litt et al [10]. These copolymers, therefore, seem to be not completely soluble in water. Consequently, the present copolymers 20 are to be regarded as a non-ionic polymeric surfactant soluble in water and to be compared with a polyether type surfactant, well-known as "Pluronics".

4. Graft Copolymer of Cellulose Diacetate Having Poly(*N*-acetylethylenimine) Graft Chains

Cellulose acetates are useful products derived from a natural polymer of cellulose. Their applications would be broadened if they could find an effective way of blending with synthetic high polymers. For this purpose, the preparation of a graft copolymer of cellulose diacetate has been accomplished by the polymerization of MeOZO with an initiator of methanesulfonate of cellulose diacetate. And, it has been found that the graft copolymer is compatible with poly(vinyl chloride)(PVC) [11].

The scheme of graft copolymerization is outlined below.



23

The degree of acetylation of the starting cellulose diacetate 21 was 2.41(=x) per one cellulose unit. A typical example of the graft copolymerization is given as follows: A mixture of 0.217 g of 22 (x = 2.41, y = 0.54) and 1.01 g of MeOZO in a PhCN/dioxane mixed solvent was kept at 90°C for 105 hr gave a MeOH-insoluble graft copolymer 23 (0.365 g after separation, n = 4.8).

Poly(MeOZO) chain has an amide structure, and hence, a weak base. It is believed that a typical commodity polymer of PVC interacts with a basic polymer via hydrogen bonding of α-hydrogen of PVC. Therefore, it is expected that the graft copolymer 23 having *N*-acetylethylenimine chain is compatible with PVC. The compatibility was examined by measuring the dynamic behavior of the film of the polymer blends with the use of a rheovibron.

Figure 4 shows elastic modulus (storage modulus) E' and loss modulus E" as a function of temperature. The E"—temperature relationship gives a better indication of compatibility because the maximum value of E" is corresponding to T_g. Curves (1) and (4) show PVC alone and the blend system of PVC and cellulose diacetate 21, respectively. The E''_{max} value is the same at 58°C in both cases, indicating that PVC and cellulose diacetate are completely incompatible with each other. Curve (3) is the graft copolymer 23 alone having E''_{max} value at 106°C. Curve (2) shows the PVC graft copolymer (23) system, in which E''_{max} is 83°C. This value is located between 58°C and 106°C and the peak is the only one observed.

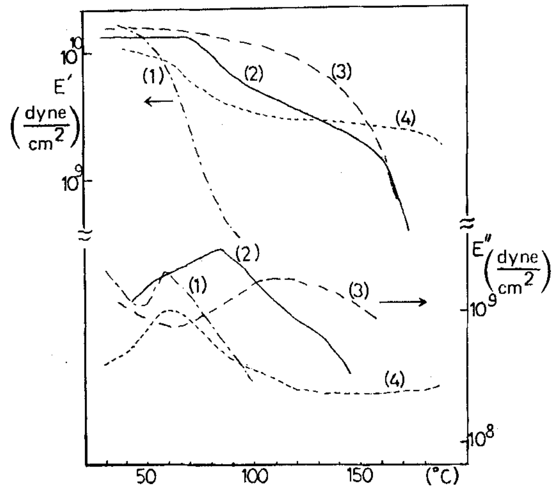


FIG. 4 Dynamic modulus (E") and loss modulus (E") versus temperature for (1) PVC, (2) blend of PVC and graft copolymer 23 (1:1), (3) graft copolymer, and (4) blend of PVC and cellulose diacetate (1:1)[11].

These results clearly indicate that the graft copolymer 23 is well compatible with PVC. Namely, *N*-acetylethylenimine chain has good function to make cellulose diacetate compatible with PVC. These properties of the graft copolymer will see a variety of applications, especially for practical use of cellulose and its derivatives.

REFERENCES

[1] T. Saegusa and S. Kobayashi, International Review of Science, Physical Chemistry Series Two, Vol. 8. Macromolecular Science, Butterworth, London, 1975, Chapter 4.
[2] T. Saegusa and S. Kobayashi, Encyclopedia of Polymer Science and Technology, Suppl. Vol. 1. Wiley, New York, 1976, p. 220.
[3] S. Kobayashi and T. Saegusa, Ring-Opening Polymerization, Applied Science Publishers LTD, Essex, England, 1983, Chapter 11.
[4] T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, *6*, 315 (1973).
[5] T. Saegusa, S. Kobayashi, and A. Yamada, Makromol. Chem., *177*, 2271 (1976).

[6] T. Saegusa, H. Ikeda, and H. Fujii, Macromolecules, *5*, 108 (1972).

[7] T. Saegusa, S. Kobayashi, and A. Yamada, Macromolecules, *8*, 390 (1975).

[8] M. Miyamoto, Y. Sano, T. Saegusa, and S. Kobayashi, Eur. Polymer J., in press.

[9] S. Kobayashi, Y. Moriuchi, T. Igarashi, and T. Saegusa, Polymer Preprints, Japan, *32*, 1475 (1983).

[10] M. H. Litt and T. Matsuda, Copolymers, Polyblends, and Composites, Adv. Chem. Ser., *142*, Am. Chem. Soc., Washington, 1975, p. 320.

[11] S. Kobayashi, M. Kaku, and T. Saegusa, Polymer Preprints, Japan, *32*, 1403 (1983).