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A Novel Silane Coupling Agent. 1. Synthesis of Trimethoxysilyl-Terminated Poly(*N*-acetylethylenimine)

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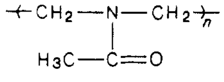
ABSTRACT: A novel type of polymeric silane coupling agent was prepared from 2-methyl-2-oxazoline. Poly(*N*-acetylethylenimine) (PAEI) with an allyl terminal group was successfully synthesized by allyl tosylate initiated polymerization of 2-methyl-2-oxazoline. The resulting propagating oxazolinium end group was reacted with various nucleophiles (2-methyl-2-oxazoline, aniline, sodium methoxide). Hydrosilylation reaction of the allyl terminal group of PAEI with trimethoxysilane produced trimethoxysilyl-terminated PAEI. On the other hand, the termination of the oxazolinium propagating end of PAEI with (3-aminopropyl)trimethoxysilane produced trimethoxysilyl-terminated PAEI. These trimethoxysilyl-terminated PAEIs were subjected to reaction with SiOH groups at the surface of silica gel. The resulting PAEI-modified silica gel showed higher hydrophilic property compared with that of untreated silica gel.

Introduction

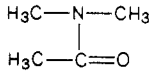
Silane coupling agents are widely used in the field of new composite materials.[1-4] Generally, a silane coupling agent consists of two components, a trialkoxysilyl group and an organic functional group. The former is reactive with silanol groups at the surface of inorganic solids such as glass. The organic group has some interactions with organic materials, especially with organic commodity polymers.

In these several years, we have been studying the ring-opening polymerization of 2-methyl-2-oxazoline.[5] The resulting poly(*N*-acetylethylenimine) (1) can be regarded as a polymer homologue of *N*,*N*-dimethylacetamide (DMAc) (2). DMAc is known as a unique solvent which has a strong affinity with water and also solubilizing ability for various organic commodity polymers. Similarly, 1 possesses high hydrophilicity and compatibility with organic polymers. Very recently,[6] we studied the miscibility of 1 with poly(vinyl chloride) (PVC) or with poly(vinylidene fluoride) (PVF_2) by means of dynamic viscoelastic behaviors, differential scanning calorimetry, and wide-angle X-ray scattering.



$-\!\left(CH_2-\underset{\underset{H_3C-C=O}{|}}{N}-CH_2\right)_{\!n}$

1



$H_3C-\underset{\underset{H_3C-C=O}{|}}{N}-CH_3$

2

Here we wish to report the synthesis of trimethoxysilyl-terminated poly(*N*-acetylethylenimines) by two methods. The first one is a hydrosilylation reaction of allyl-terminated poly(*N*-acetylethylenimine) with trimethoxysilane. The other method consists of the termination of propagating oxazolinium species with (3-aminopropyl)trimethoxysilane. Taking account of the characteristic properties of poly(*N*-acetylethylenimine) described above, these trimethoxysilyl-terminated poly(*N*-acetylethylenimines) are taken to be useful as a novel type of silane coupling agent.

Experimental Section

Materials and Instruments. Allyl *p*-toluenesulfonate (allyl tosylate) (4) was prepared according to the method reported previously for butyl p-toluenesulfonate.[7] 2-Methyl-2-oxazoline (3), trimethoxysilane, (3-aminopropyl)trimethoxysilane (13), aniline, and all solvents were dried and distilled under nitrogen. Sodium methoxide was prepared from sodium with methanol. Silica gel (15) was obtained from Merck Co. (Merckogel, Art9381).

IR spectra were obtained on a Hitachi 260-50 grating spectrophotometer. The ^1H NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-20B (60-MHz) instrument. Gas chromatographic analysis (GC) was made on a Shimadzu GC-6A instrument. GPC analysis was carried out on a Toyo-Soda CCPD (TSK gel G2500) after calibration with standard poly(*N*-acetylethylenimine) samples.

Allyl Tosylate (4). To a mixture of allyl alcohol (14.5 g, 0.25 mol) and *p*-toluenesulfonyl chloride (tosyl chloride) (26.7 g, 0.14 mol) in a 500-mL three-necked flask equipped with a thermometer and a dropping funnel was added 5 N aqueous sodium hydroxide solution (80 mL) below 15 °C. Additional tosyl chloride (26.6 g, 0.14 mol) and then 5 N aqueous NaOH (80 mL) were added consecutively to the reaction mixture. An organic layer was extracted with benzene, washed with 10% aqueous NaOH, and then dried over potassium carbonate. Evaporation of solvent produced liquid allyl tosylate (4). 4 was purified by distillation (110 °C, 0.15 mmHg), yield 18.9 g (36%). From ^1H NMR analysis, the purity of 4 was higher than 95% and was found to be good enough for the following ring-opening polymerization of 2-methyl-2-oxazoline as an initiator.

Allyl-Terminated PAEI (5). In a typical procedure, a mixture of 2-methyl-2-oxazoline (3) (2.89 g, 34.0 mmol), allyl tosylate (4) (0.85 g, 4.00 mmol), and acetonitrile (10 mL) was placed in a 50-mL flask with a reflux condenser and heated at 60 °C for 13 h under nitrogen. The resulting allyl-terminated PAEI (5) was used in situ for the following reactions with some nucleophiles.

Reactions of 5 with Nucleophiles. Aniline (0.45 g, 4.83 mmol) was added to the resulting 5 described above, and the reaction mixture was stirred at room temperature for 21 h. The reaction mixture was treated with ion-exchange resin (Amberlyst A-21), and the resulting aniline-terminated PAEI (7) was isolated by reprecipitation (chloroform to *n*-hexane) followed by freeze-drying with benzene, yield 3.41 g (100%).

By use of a similar procedure, the reaction of 5 with 2-methyl-2-oxazoline or with sodium methoxide was carried out. Products 6 and 8 + 9 (10), respectively, were obtained and characterized by their ^1H NMR spectra.

Hydrosilylation Reaction of 5 with Trimethoxysilane. In a typical procedure, a mixture of allyl-terminated PAEI (5) (degree of polymerization by ^1H NMR 7.5, 1.08 g, 1.40 mmol), chloroplatinic acid catalyst (3.74×10^{-5} mmol), and acetonitrile (10 mL) was placed in a 50-mL flask equipped with a reflux condenser. Trimethoxysilane (1.16 g, 9.49 mmol) was added dropwise, and the reaction mixture was stirred at 60 °C for 12 h under nitrogen. Trimethoxysilyl-terminated PAEI (11) was obtained and purified by reprecipitation.

The hydrosilylation reaction of 7 with trimethoxysilane was carried out according to a procedure similar to that used to obtain trimethoxysilyl-terminated PAEI (12).

Termination of PAEI Propagating End with (3-Aminopropyl)trimethoxysilane. Under nitrogen, a mixture of 2-methyl-2-oxazoline (3) (2.02 g, 23.7 mmol), allyl tosylate (4) (1.50 g, 8.05 mmol), and acetonitrile (10 mL) was placed in a 50-mL flask equipped with a reflux condenser and stirred at 60 °C for 4 h. Then, (3-aminopropyl)trimethoxysilane (13) (2.12 g, 9.58 mmol) was added to the reaction mixture at 0 °C. The resulting reaction mixture was stirred at room temperature for 20 h followed by treatment with an ion-exchange resin of Amberlyst A-21.

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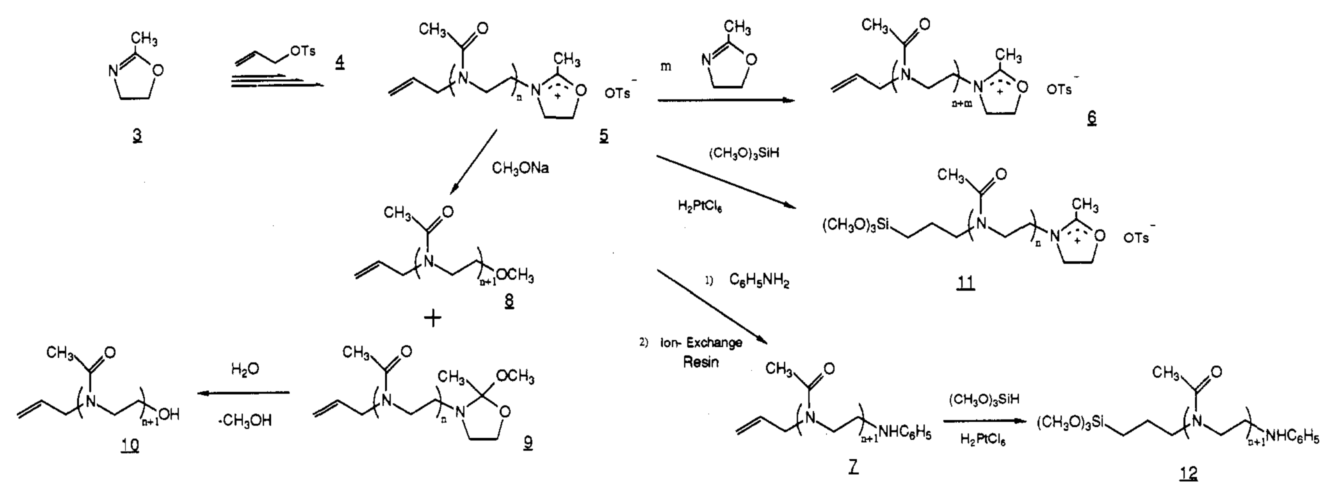
Scheme I



Trimethoxysilyl-terminated PAEI (14) was isolated by reprecipitation and drying in vacuo, yield 3.61 g (92% based on the starting 2-methyl-2-oxazoline).

Treatment of Silica Gel with 12 or 14. Silica gel (0.34 g) and trimethoxysilyl-terminated PAEI (12) (acetonitrile solution) were placed in a 5-mL glass ampule and heated under reflux for 9 days. The resulting silica gel was purified by Soxhlet extraction with chloroform to remove unreacted trimethoxysilyl-terminated PAEI. The content of PAEI in silica gel was 9.67 wt % determined by elemental analysis.

Results and Discussion

Synthesis of Allyl-Terminated PAEI (5). As shown in Scheme I, allyl-terminated poly(*N*-acetylethylenimine) (PAEI 5) was prepared successfully by ring-opening polymerization of 2-methyl-2-oxazoline (3) with allyl tosylate initiator (4) in acetonitrile at 60 °C. 4 was synthesized from allyl alcohol and tosyl chloride according to the reported procedure for the preparation of *n*-butyl tosylate.[7] After distillation, the obtained 4 was pure enough as an initiator for the ring-opening polymerization of 3. Figure 1A illustrates the ^{1}H NMR spectrum of the product polymer 5, which was purified by reprecipitation in diethyl ether. The degree of polymerization (n) of 5 can be calculated from the integral ratio of vinyl protons (δ 5.26 and 5.61 ppm, 3 H) to methyl protons (δ 2.09, 2.37, and 2.47 ppm, $(3n + 3 + 3)$ H). This value was close to that calculated from the feed ratio of initiator 4 to monomer 3. In other words, the functionality of allyl group in the resulting polymer, 5, was nearly unity. The peaks at δ 2.37, 2.47, 4.00, 4.43, and 7.45 ppm, which are assignable to the protons of oxazolinium tosylate at the propagating end, were also observed in the ^{1}H NMR spectrum of 5. From the integral ratio of vinyl protons to aromatic protons of tosylate anion (δ 7.45 ppm, 4 H), the ratio between allyl group at the initiating end and the oxazolinium tosylate at the propagating end was almost unity. This result indicates the polymerization proceeded *via* living mechanism and the active propagating species (oxazolinium) still remained unchanged at the terminal even after the isolation of 5. Table I summarizes the results of preparation of 5. In all cases, the conversions of 3 were almost quantitative. As can be seen in Table I, the molecular weights of 5 were easily controlled by the feed ratio of 3 to 4.

Reactions of 5 with Nucleophiles. The terminal oxazolinium group in 5 can be reacted with various nucleophiles. Thus, three kinds of nucleophiles, i.e., 2-methyl-2-oxazoline (3), aniline, and sodium methoxide, were examined as summarized in Scheme I. The additional ring-opening polymerization of 3 initiated by 5 ($\bar{M}_n$ = 500) took place in acetonitrile at 60 °C to produce allyl-terminated PAEI (6, $\bar{M}_n$ = 1000). From the results of GPC analysis, the efficiency of initiation by 5 was almost quantitative. This result also shows that the oxazolinium salt, which is the active propagating species in the polymerization of 3, remained unchanged at the end of 5. It is reasonably assumed that ring-opening polymerization of 2-alkyl-2-oxazoline (alkyl = H, ethyl, and higher carbons)

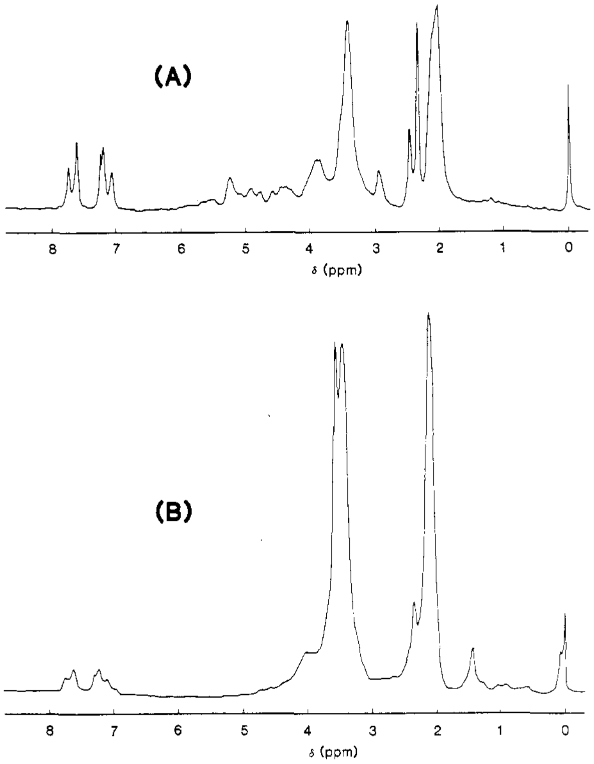


Figure 1. ^{1}H NMR spectra of (A) allyl-terminated (5) and (B) trimethoxysilyl-terminated (11) poly(*N*-acetylethylenimine)s.

Table I
Preparation of Allyl-Terminated PAEI 5

run	[3]/[4][a]	time, h	temp, °C	5 yield, %[b]	5 DP[c]	5 $\bar{M}_n$[d]
1	5.1	4.5	60	70	4.9	630
2	4.7	5.0	60	72	4.9	650
3	4.5	5.5	60	72	4.5	590
4	4.6	9.5	80	74	4.3	570
5	10.0	5.0	70	72	9.3	1000
6	2.9	5.5	60	74	3.5	510

[a] Feed ratio of 3 to 4. [b] Isolated yield after reprecipitation. [c] Degree of polymerization was determined by ^{1}H NMR analysis. [d] Calculated from ^{1}H NMR.

Table II
Preparation of Trimethoxysilyl-Terminated PAEI 11

run	5		(MeO)$_3$SiH, g	yield,[b] %	conversion,[c] %
	DP[a]	g			
1	3.5	2.13	5.12	82	80
2	4.3	0.63	1.50	71	70
3	4.9	0.28	1.13	54	60
4	9.3	0.89	0.56	69	60
5	9.3	1.73	4.59	75	100

[a] Degree of polymerization was determined by ^{1}H NMR analysis. [b] Isolated yield after reprecipitation. [c] Conversion from allyl group to trimethoxysilyl group was calculated by ^{1}H NMR analysis.

by **5** produces allyl-terminated polyoxazoline block copolymers.

The reaction of **5** with aniline took place in acetonitrile at room temperature. This means the termination of polymerization of **3** by aniline. The nucleophilic attack of aniline to the carbon adjacent to oxygen atom of oxazolinium in **5** produced anilinium group. The resulting polymer was treated with ion-exchange resin for the conversion from anilinium salt to N-substituted aniline. Thus, the telechelic functional (allyl group at one end and phenylamino group at another end) PAEI (**7**) was obtained by this method. The molecular weight of **7** was 600, which is in good agreement with that calculated from the molecular weight of the starting PAEI, **5** ($\bar{M}_n$ = 500).

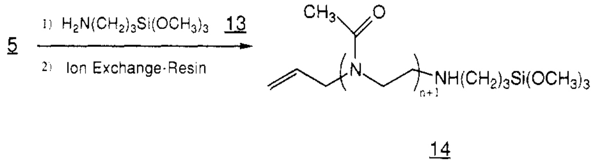
A nucleophile stronger than aniline, such as sodium methoxide, was used for the reaction with the oxazolinium of **5**. However, in this case, sodium methoxide can attack both the 2-position and 5-position of oxazolinium to form **8** and **9**, respectively. The ratio of **8** to **9** was 30:70 from the results of ^{1}H NMR analysis. During the isolation procedure, i.e., reprecipitation and washing, the resulting ketal group in **9** was hydrolyzed with moisture in air to produce hydroxyl-terminated PAEI (**10**). As a result, two telechelic PAEIs (allyl and methoxy termini, allyl and hydroxyl termini) were obtained as a mixture of **8** and **10** (30:70) by reaction of **5** with sodium methoxide.

Synthesis of Trimethoxysilyl-Terminated PAEI. Hydrosilylation Method. Hydrosilylation reaction of hydrosilane compounds to double bond is well-known in organic synthesis. The reaction of the allyl group of **5** and trimethoxysilane with chloroplatinic acid catalyst was carried out in 1,2-dichloroethane at 100 °C under nitrogen. Figure 1 illustrates ^{1}H NMR spectra of **5** (A) and the resulting trimethoxysilyl-terminated PAEI **11** (B). After the hydrosilylation reaction, vinyl protons of **5** disappeared and methoxy protons of **11** appeared in Figure 1B. From the integral ratio, the conversion of allyl group into trimethoxysilyl group can be calculated. The results of the preparation of **11** are summarized in Table II. Use of a large excess of trimethoxysilane (run 5 in Table II) causes the conversion of **5** into **11** to be almost quantitative.

The terminal allyl group of aniline-terminated PAEI (**7**) was also subjected to the hydrosilylation reaction with trimethoxysilane. From ^{1}H NMR analysis, the conversion from allyl group to trimethoxysilyl group was almost 100%. The obtained trimethoxysilyl-terminated PAEIs (**11** and **12**) can be used as a silane coupling agent.

Synthesis of Trimethoxysilyl-Terminated PAEI. Termination Method. As described above, the active oxazolinium propagating species in ring-opening polymerization of 2-methyl-2-oxazoline receives a nucleophilic attack by amine. Here, the direct introduction of trimethoxysilyl group to PAEI was examined by the termination method. As shown in Scheme II, allyl tosylate initiated ring-opening polymerization of **3** produced PAEI **5**. Again in polymer **5**, the oxazolinium salt remained at the polymer end, which was reacted with (3-aminopropyl)trimethoxysilane (**13**). After the treatment with ion-exchange resin, trimethoxysilyl-terminated PAEI **14** was isolated. The structure of **14** was examined by ^{1}H NMR spectra, from which the terminal trimethoxysilyl group was found to be effectively introduced to PAEI. The present polymer, **14**, can also be used as a novel polymeric silane coupling agent.

Scheme II



Scheme III

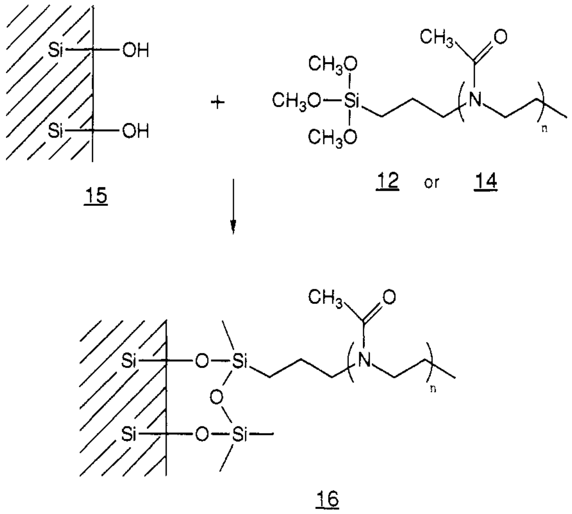


Table III
Treatment of Silica Gel with 12 or 14

run	PAEI			PAEI in 16, wt %[c]	H$_2$O content[d]
	compd	$\bar{M}_n$[a]	wt %[b]		
1			0[e]	0	10.8
2	12	770	49	9.7	13.7
3	14	710	52	8.7	[f]
4	14	710	55	10.3	11.6

[a] Calculated by ^{1}H NMR analysis. [b] wt % of PAEI in feed. [c] Calculated by elemental analysis. [d] g of H$_2$O/g of dried **16**. [e] Silica gel alone (**15**). [f] Not determined.

Silane Coupling of Silica Gel. As illustrated in Scheme III, the reaction of trimethoxysilyl-terminated PAEI (**12** or **14**) and the silanol group of silica gel (**15**) was examined in order to demonstrate the usefulness of the present novel silane coupling agent. For example, **12** and **15** were heated in acetonitrile under nitrogen. The resulting silica gel was subjected to Soxhlet extraction with chloroform to remove unreacted PAEI **12**. From the results of elemental analysis, PAEI segments were found to have been easily introduced to the surface of silica gel. From *N*% of the resulting modified silica gel, **16**, the content of the PAEI segment can be calculated. Table III summarizes these results.

The dried PAEI-modified silica gel **16** was immersed into distilled water. The swelling property of the resulting gel was estimated by the water content. The water uptake was calculated from the equation of $(W' - W)/W$, where W is the weight of dried **16** and W' is the weight of swollen **16**. As shown in Table III, **16** shows a higher water-swollen property than that of untreated silica gel, **15**, which absorbs 10.8 multiples of water. The water uptake of **16** was up

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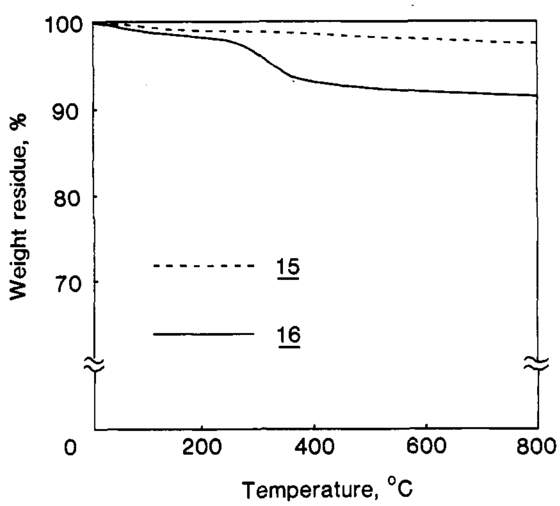

Figure 2. TGA of PAEI-modified silica gel (**16**, —) and untreated silica gel (**15**, - - -).

to 13.7 multiples of the weight of dried **16**. Thus, silica gel has been made more hydrophilic by a PAEI segment.

Figure 2 shows the result of thermogravimetric analysis, in which the weight loss of the resulting PAEI-modified silica gel (**16**, run 2 in Table III) started at 230 °C; the weight was nearly 90% above 400 °C under nitrogen. The amount of weight loss at 400 °C is comparable with the PAEI content of **16** determined from elemental analysis. In other words, **16** lost its PAEI moiety at 400 °C.

Conclusions

Two ways have been established for the preparation of trimethoxysilyl-terminated PAEIs. As mentioned in the Introduction, PAEI has useful characteristics, i.e., hydrophilicity and good compatibility with other organic commodity polymers. Taking account of these characteristics, the polymer obtained in the present study can be used as a novel type of silane coupling agent. In fact, silica gel was made more hydrophilic by these polymeric silane coupling agents. Generally, polyoxazolines have a wide spectrum from hydrophilic to lipophilic nature depending on the *N*-acyl groups. For example, the polymer from 2-methyl-2-oxazoline shows high hydrophilicity, and the polymers from higher alkyl derivatives (butyl or higher) show hydrophobicity (lipophilicity). Accordingly, trialkoxysilyl-terminated polymer from 2-alkyl-2-oxazoline can be used to modify lipophilic silica gel. The subject will be the next target of our research. Polyoxazolines also have high compatibility with organic commodity polymers such as poly(vinyl chloride). This property makes it possible to produce a new composite material, in which polyoxazoline reinforces the interface between organic polymers and inorganic materials. Reinforcement by polyoxazoline silane coupling agent is now under investigation.

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Registry No. 4, 4873-09-0.

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Liquid Crystal Polyethers Containing Macroheterocyclic Ligands. 1. Polyethers and Copolyethers Based on 4,4′-Dihydroxy-α-methylstilbene, Bis(8-bromooctyl)dibenzo-18-crown-6, and/or 1,11-Dibromoundecane

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ABSTRACT: The synthesis and characterization of the first examples of thermotropic main-chain liquid-crystalline polyethers and copolyethers containing macroheterocyclic ligands is described. The particular example presented in this paper refers to polyethers and copolyethers based on bis(8-bromooctyl)dibenzo-18-crown-6 and/or 1,11-dibromoundecane and 4,4′-dihydroxy-α-methylstilbene. The polyether based on 4,4′-dihydroxy-α-methylstilbene and 1,11-dibromoundecane displays an enantiotropic nematic mesophase while the one based on 4,4′-dihydroxy-α-methylstilbene and bis(8-bromooctyl)dibenzo-18-crown-6 is crystalline. Copolyethers containing up to as much as 60 mol % dibenzo-18-crown-6 structural units display a monotropic nematic mesophase. Both liquid-crystalline transition temperatures and the corresponding enthalpies of the copolymers are weight-averaged values of the parent homopolymers. Extrapolation of the monotropic nematic transition temperatures and their enthalpy changes have demonstrated that all copolymers and the homopolymer based on 4,4′-dihydroxy-α-methylstilbene and bis(8-bromooctyl)dibenzo-18-crown-6 exhibit a virtual monotropic nematic mesophase. The thermal transition temperatures and the enthalpy changes associated with the virtual nematic mesomorphic transitions of the homopolymer and the copolymer were determined.

Introduction

Since the discovery of crown ethers,[1] the field of host guest complex chemistry has received tremendous research interest[2] and recently definitive scientific recognition.[1,3] However, to our knowledge, there are only two examples of low molar mass liquid crystals containing macroheterocyclic ligands. The first one refers to disclike amide derivatives of macrocyclic polyamines which exhibit co-

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