NOTE

Dipole Moments of Poly(oxypropylene), Poly[(S)-oxy(1-isopropylethylene)] and Their Monomeric Model Compounds

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Dipole moment is one of the fundamental physical properties which provides important information regarding the conformation of polymer chains having polar skeletal bonds.¹ We have been studying the conformational characteristics of a series of poly[oxy(1-alkylethylene)]s carrying side chains such as methyl, ethyl, isopropyl, and *t*-butyl groups.^{2,3} In this note, we wish to report the experimental values of the dipole moment for poly(oxypropylene) and poly[(S)-oxy(1-isopropylethylene)]. The results of our investigation on the low molecular weight model compounds, 1,2-dimethoxypropane and (S)-1,2-dimethoxy-3-methylbutane, are also included.

Dipole moments μ were calculated from the observed dielectric constants (at 2 and 1 MHz for μ 's in Tables I and II, respectively) and densities of the solutions according to the Halverstadt-Kumler method.^{4,*} The results are summarized in Tables I and II. Shown in the last columns are the mean-square dipole moment ratios $\langle \mu^2 \rangle / nm^2$, where n is the

number of skeletal bonds and m^2 is the averaged value of the squares of the bond dipole moments. In these calculations, the bond dipole moments for the C—O and the C—C bonds were assumed to be 1.07 and 0 Debye, respectively.^{2,3,8}

The dipole moment of poly(oxypropylene) is larger in benzene than in cyclohexane by about 5%. Enhancement of the dipole moment at a similar magnitude was found for the model compound as well. The temperature coefficients $d \ln \langle \mu^2 \rangle / dT$ estimated within the range 25—50°C are positive, but small in magnitude for both poly(oxypropylene) [$0.7 (\pm 1.0) \times 10^{-3} \text{K}^{-1}$] and its model compound [$0.5 (\pm 0.5) \times 10^{-3} \text{K}^{-1}$].

Poly[(S)-oxy(1-isopropylethylene)] shows a higher dipole moment than poly(oxypropylene). The mean-square dipole moment ratio $\langle \mu^2 \rangle / nm^2$ of poly[(S)-oxy(1-isopropylethylene)] is about twice as large as that of its model compound, while the value of $\langle \mu^2 \rangle / nm^2$ varies little between poly(oxypropylene) and its low molecular weight analog.

A detailed analysis of the polymer conformations will be reported elsewhere.^{2,3}

* Equation $\mu = 0.0128 \sqrt{(P_2 - 1.05MR_D)T}$ is used for the calculation of μ ; P_2 , MR_D and T are the molar polarization from the Halverstadt-Kumler method,^{4b} the molar refractivity calculated as the sum of atomic refractivities and the absolute temperature, respectively.

Table I. Dipole moments of poly(oxypropylene) and its monomeric model 1,2-dimethoxypropane

Compound	Solvent	Temp/°C	Dipole moment ^a	$\langle\mu^2\rangle/\text{nm}^2$
			Debye	
Poly(oxypropylene) ^b	Cyclohexane	25	1.04	0.47
	"	35	1.04	0.47
	"	51	1.05	0.48
	Benzene	25	1.09	0.52
	"	35	1.09	0.52
	"	51	1.10	0.53
1,2-Dimethoxypropane	Cyclohexane	23.4	1.57	0.54
	"	36	1.57	0.54
	"	51	1.58	0.55
	Benzene	23.2	1.64	0.59
	"	25	1.65	0.59
	"	36	1.65	0.59
	"	51	1.66	0.60

^a For a polymer, given as the dipole moment per monomeric residue. Experimental error: ± 0.03 Debye for polymer and $\pm 0.01 \sim 0.02$ Debye for the monomeric model.

^b Acetone-insoluble part (fractionation: 0.02 g cm^{-3} in acetone at -20°C) of crude polymer obtained by the polymerization of (*RS*)-methyloxirane with $\text{Zn}(\text{C}_2\text{H}_5)_2\text{-CH}_3\text{OH}$ (1:1.7 in mole ratio) catalyst (5 mol% to monomer) in benzene (1:1 in volume ratio to the monomer) at 30°C for 14 h. A polymer sample obtained in this manner is highly isotactic.⁵

Table II. Dipole moments of poly[(*S*)-oxy(1-isopropylethylene)], P(*S*-OIPE), and its monomeric model (*S*)-1,2-dimethoxy-3-methylbutane

Compound	Solvent	Temp/°C	Dipole moment ^a	$\langle\mu^2\rangle/\text{nm}^2$
			Debye	
P(<i>S</i> -OIPE) A ^b	Benzene	25	1.4 ₃	0.89
P(<i>S</i> -OIPE) B ^c	"	25	1.3 ₈	0.83
(<i>S</i>)-1,2-Dimethoxy-3-methylbutane	"	25	1.44 ± 0.03^d	0.45

^a For a polymer, given as the dipole moment per monomeric residue.

^b Methanol-insoluble fraction of the polymer obtained by the polymerization with amorphous $\text{Zn}(\text{OCH}_3)_2$ catalyst in a way similar to that reported previously.⁶

^c Methanol-insoluble fraction of the polymer obtained by the polymerization with $\text{Zn}(\text{C}_2\text{H}_5)_2\text{-H}_2\text{O}$ (1:0.8 in mole ratio) catalyst in the same way as reported previously.⁷

Although not determined for the present samples, the molecular weight of P(*S*-OIPE) B should be much higher than that of P(*S*-OIPE) A.^{6,7}

^d Measured at 2 MHz.

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