Colloid Science

Liquid properties of oligomers. Comparison of relaxational properties of propylene glycol oligomers with those of ethylene glycol oligomers

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Abstract: Liquid properties such as dielectric relaxation and viscous flow of the two structurally homologous propylene glycol oligomers $HO(CH(CH_3)CH_2O)_nH$ ($n = 1, 2, 3, 4, 5$ and 34) and ethylene glycol oligomers $HO(C_2H_4O)_nH$ ($n = 1, 2, 3, 4, 5$ and 6) are studied in pure liquid state to clarify the degree of polymerization dependences of chain molecules on their liquid properties. These oligomers are, at room temperature, viscous liquid which shows dielectric relaxations in the frequency range from 10 Hz to 3 MHz. Propylene glycol oligomers ($n =$ from 1 to 5) show the Davidson-Cole-type relaxations, but the higher glycol ($n = 34$) shows superposition of the two different relaxations, i. e., small Debye-type relaxation in the lower-frequency region and large principal Havriliak-Negami-type relaxation in the higher-frequency region. Relaxation times vs. degree of polymerization do not increase linearly, but vary in zigzag lines. Above all, the dimers (dipropylene glycol and diethylene glycol) show longer relaxation times than the other glycols. This dielectric result does not agree with the degree of polymerization dependence of viscous flow.

Key words: Diol oligomers, pure liquid state, dielectric properties, degree of polymerization dependences, ring formation of dimer.

Introduction

At present it is still very difficult to relate quantitatively the macroscopic properties shown by a long chain molelcule to its chemical structure. For example, theoretical calculation of its dipole moment involves determination of somewhat arbitrary parameters such as potential barrier for intramolecular rotation and tedious mathematical calculation. It seems, therefore, desirable to investigate properties of the oligomers to avoid the complexities characteristic of the polymeric system. The principal dielectric relaxation of polymers in a rubbery state is due to microbrownian motion of chain segment since molecular flow does not occur. So only limited rotation, i. e., microbrownian motion of chain segment is possible in the so-called "free volume". On the other hand, principal dielectric relaxation of a polar small molecule like acetone in a liquid state is attributed to the molecular rotation as a whole. Thus the motional mode in the relaxational mechanism changes from molecular rotation to segmental motion with increasing chain length. Widening distribution of relaxation times with increasing chain length for n-alkyl bromides was reported by Hennelly et al. [1]. It is, however, difficult to find out the critical chain length of this motional transition because this translation must occur gradually with increasing chain length. It is expected that the dielectric studies on the oligomers, which are intermediates between small molecules and polymers, give information about the motional translation.

From this viewpoint, the degree of polymerization dependences on dielectric properties of oligomers has been investigated by varying their chain length.

Mead and Fuoss reported that the relaxational arcs on the Cole-Cole plane of polyvinylacetate were asymmetric [2]. The calculated arcs of the Davidson-Cole equation resemble well the asymmetric arcs of polyvinylacetate [3]. The dielectric properties of the

vinylacetate oligomers and the related acetate molecules were investigated in detail to clarify the chain length dependences of the relaxational behaviors of vinylacetate molecules [3, 4, 5, 6]. The liquid and the supercooled polyhydroxy compounds show the asymmetric Davidson-Cole-type relaxation [7, 8, 9]. It is mathematically proved that the asymmetric distribution of relaxation times is associated with the cooperative mechanism of dielectric relaxation [10]. Above all, the apparent similarity in the relaxation phenomena between the principal relaxation of the polymer and of polyhydroxy compounds is very interesting.

Davidson and Ikada studied the dielectric properties of isomeric pentanediols [8] and of $HOC_2H_4X-C_2H_4OH$ (X = -NH-, -S-, -O- and -CH_2-) [9] respectively to clarify the molecular structure dependences on the relaxational mechanism showing this type of relaxation. Ikada studied the effects of hydrogen bonds on the Davidson-Cole-type relaxations of diols by the substitution of hydroxyl group with non hydrogen bonding group [3].

Koizumi and Hanai studied the dielectric relaxation of ethylene glycol oligomers with a degree of polymerization between 1 and 7 in a liquid state [11, 12]. Propylene glycol oligomers, having a chemical structure similar to that of ethylene glycol oligomers are also one important type of commercial oligomers, and remain liquid even for oligomers of molecular weight greater than 2000. Needless to say, the most marked difference in molecular structure between ethylene and propylene glycol oligomers is the existence of a methyl group in the repeating unit of the latter oligomers, melting points of which, however, are much lower than those of the former oligomers, probably because of the additional entropy caused by the methyl group.

The purpose of this study is to investigate the relationship between the dielectric properties and the molecular structures of oligomers, to explain variations of relaxation mechanisms with increasing chain length.

Experimental

Propylene glycol oligomers (n = 1, 2, 3, 4, 5 and average degree of polymerization = 34) are obtained by the following method. According to gaschromatographic analysis, the commercial product PPG-diol 400 (Mitsui-Nisso Urethane Co.) is mixture of trimer, tetramer, pentamer and hexamer [13]. Each pure component was obtained by fractional distillation under reduced pressure (ca. 0.05 – 0.07 Torr). Purity was ascertained by gaschromatography. PPG-diol 2000 was used as an oligomer with higher molecular weight. Hereafter, the name of this diol is abbreviated as PPG. The

molecular weight of this diol is 1980. The non-hydrogen bonding diol was obtained by acetylation with acetic anhydride [14]. This molecule is named as PPGA. PPG-diol 400 and 2000 were kindly given by Mitsui-Nisso Urethane Co. Ethylene glycol oligomers for viscosity, density and infrared measurement are commercial products.

Dielectric measurement

Dielectric constants and losses were measured with a ratio-arm transformer bridge (type TR-1BK, Ando Electric Co.) with a frequency range from 10 Hz to 3 MHz. Dielectric cell is a concentric platinum glass cell. The vacuum capacitance was determined by standard dielectric liquids. Temperature was controlled by water and alcohol baths. The dipole moment in carbon tetrachloride was measured by the dilute solution method [15] with a precision capacitance bridge (system 1621, General Radio). The molar refraction was determined by adding the atomic refractions.

Measurement of density and viscosity

Densities of the oligomers were measured with a Lypkin-type pycnometer calibrated with water. Viscosities were measured with a falling-ball-type viscometer for highly viscous liquids and with an Ostwald-type viscometer for low viscosity liquids.

Infrared spectroscopy

Infrared spectra of carbon tetrachloride solution were observed with an infrared spectrometer (type DS-701 G, JASCO Co.). Integrated strength of infrared absorption A was calculated by the following equation:

$$kpl = \ln (I/I_0) \text{ and } A = \int k(v)dv = \frac{1}{pl}\int \ln (I/I_0)dv$$

where $k(v)$ is molar absorption coefficient for characteristic frequency v and p is concentration of the sample and l is length of the cell. I_0 and I are the intensities of incident light and the light passing through l, respectively. Analysis of the absorption curves was carried out by a wave analyzer (type 310, du Pont).

Results and discussion

Static dielectric constant

The static dielectric constants of ethylene and propylene glycol oligomers against reciprocals of absolute temperatures are shown in Figure 1. Good linear relationship is seen even for large and small static dielectric constants. Of all the diols measured, the static dielectric constants of the monomers and of the dimers are large because of the effect of regular molecular orientation due to intermolecular hydrogen bond. On the
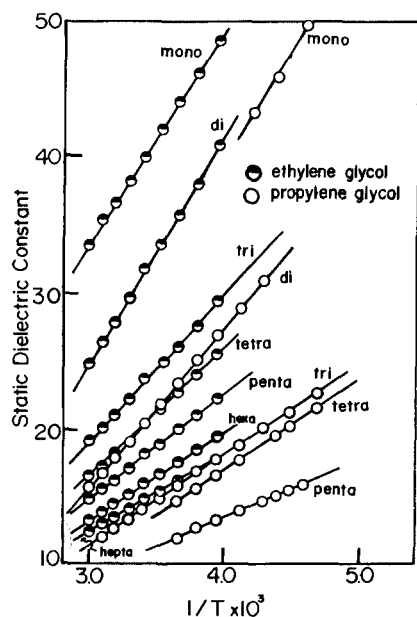
Fig. 1. Static dielectric constants vs. reciprocal absolute temperatures. Data on monopropylene glycol, dipropylene glycol, and all the ethylene glycols (●) from References [14], [8], and [9], respectively. ○ denotes propylene glycol

Fig. 3. Densities of glycol and glycol diacetate oligomers: Curve 1, triethylene glycol; 2, diethylene glycol; 3, monoethylene glycol; 4, monopropylene glycol diacetate; 5, dipropylene glycol diacetate; 6, tripropylene glycol diacetate; 7, monopropylene glycol; 8, dipropylene glycol; 9, tripropylene glycol

other hand, the values of static dielectric constant of pentapropylene glylcol are as small as the values of a normal liquid. This result clearly shows that the cluster formation by hydrogen bond decreases with the increasing chain length because the number of OH end
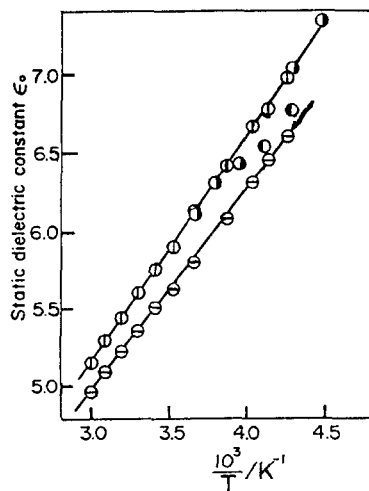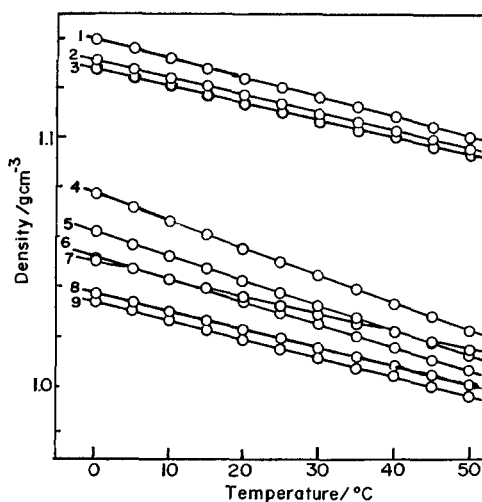

Fig. 2. Static dielectric constants vs. reciprocal absolute temperatures. PPG: this work (◐); Baur-Stockmayer's data [15] (●). PPGA: this work (⊖); Baur-Stockmayer's data [15] (◑)

groups per unit volume decreases. To know the contribution of hydrogen bond to the static dielectric constant more precisely, the static dielectric constants of PPG having OH end groups are compared with those of PPGA having CH_3COO end groups in Figure 2. As is seen in figure, the static dielectric constants of the former are slightly larger than those of the latter and this small difference is regarded as resulting from the local regularity.

It is found in Figure 1 that the static dielectric constants of ethylene glycol oligomers are larger than those of propylene glycol oligomers for the same degree of polymerization. Such difference results from the difference of dipole moment, or number of dipoles per unit volume or effective dipolar orientation due to hydrogen bond between the two homologues. Figure 3 shows temperature dependences of the densities for both diols. As is seen in this figure, the densities of ethylene glycol oligomers are larger than those of propylene glycol oligomers although the molecular weight of the repeating unit of propylene glycol oligomers is larger than that of ethylene glycol oligomers. The comparison of molecular weights suggests that the densities of the former oligomers should be larger than those of the latter ones, but the result was contrary to this expectation.

The difference of dipole moment between the two oligomers is small, as is shown in Table 1. Therefore,

Table 1. Dipole moments of propylene and ethylene glycols (Debye units)

	Propylene glycols (at 20°C)	Ethylene glycols[a] (at 25°C)
Monomer	2.50	2.38
Dimer	–	2.69
Trimer	3.02	2.99
Tetramer	3.08	3.25
Pentamer	3.28	3.42

[a]) Uchida T, Kurita Y, Koizumi N, Kubo M (1956) J Polym Sci 21:313

Fig. 4. Cole-Cole plots for pentapropylene glycol at various temperatures

the difference of the static dielectric constants cannot be explained by their dipole moments. Also the decreasing static dielectric constants with the increasing chain length are not associated with their dipole moments since the dipole moments increase with the increasing chain length.

The difference between the static dielectric constants of the ethylene and propylene glycol oligomers must result either from the larger number of molecules per unit volume or from larger local regularity due to hydrogen bond in the liquid structure of the ethylene glycol oligomers.

Dielectric relaxations of the oligomers

Liquid propylene glycol oligomers show dielectric dispersion and absorption in the measured frequency range. Davidson and Cole reported that the experimental skewed arcs of monopropylene glycol are represented by the following Equation [16]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau_0)^\beta} \qquad (1)$$

where ε^* is the complex dielectric constant, ε_0 and ε_∞ are the limiting low- and high-frequency dielectric constant, respectively. j is $\sqrt{-1}$ and ω is the angular frequency; τ_0 is the average relaxation time and β is the distribution parameter of relaxation times.

Figure 4 shows the Cole-Cole plots of pentapropylene glycol. This very large glycol is a pentamer of propylene glycol as follows:
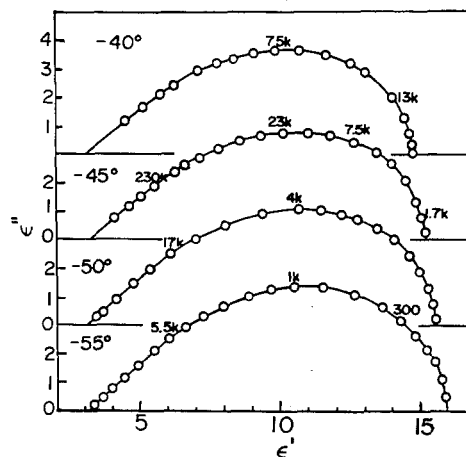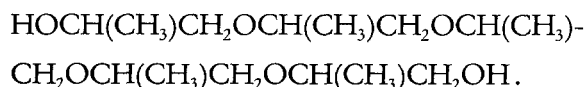
HOCH(CH₃)CH₂OCH(CH₃)CH₂OCH(CH₃)-

CH₂OCH(CH₃)CH₂OCH(CH₃)CH₂OH .

The observed asymmetric experimental arcs of the propylene glycol oligomers from the dimer to the pentamer are analyzed by Equation (1). Agreement between the experimental arcs and the arc calculated by using Equation (1) is good and the obtained distribution parameters are collected in Table 2.

On the other hand, a much longer diol PPG shows flatter Cole-Cole arcs than the above-mentioned propylene glycol oligomers do, as shown in Figure 5. As is clearly seen in this figure, the dielectric relaxation of this long PPG chain shows existence of the two separate relaxations, a small sub-relaxation expressed by the Debye Equation in the lower frequency region and a large principal relaxation in the higher frequency region. This skewed arc agrees well with the calculated curves using the following Havriliak-Negami Equation [10]:

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau_0)^{1-\alpha}]^\beta} \qquad (2)$$

where $1-\alpha$ is another distribution parameter of relaxation times. The calculated values for $1-\alpha$ and β of the principal relaxations are collected in Table 2.

Baur and Stockmayer attributed this small Debye-type absorption to the dielectric relaxation of a "cumulative" dipole along a main chain, about 0.18 D per monomer unit, whose resultant magnitude depends on the long-range conformation of the chain molecule [17]. As is clearly seen in Figure 4, this small relaxation
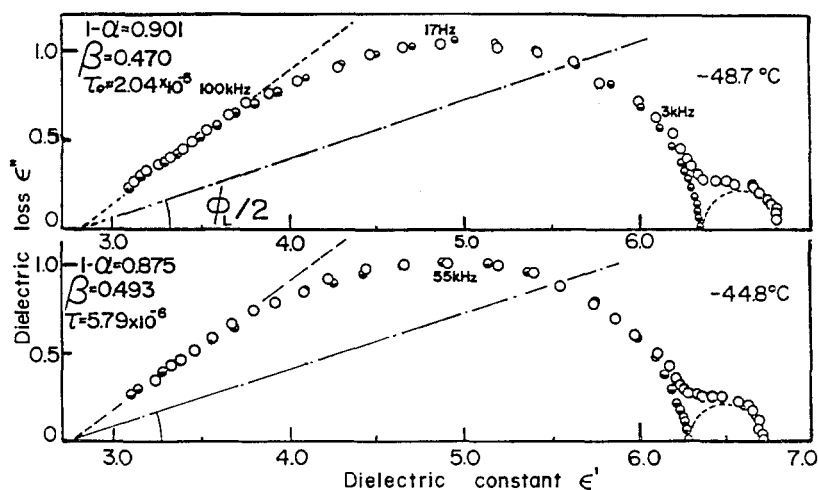
Fig. 5. Cole-Cole plots of the complex dielectric constants of propylene glycol oligomer PPGA: ϕ_L is the angle between the asymptote in the high-frequency region of the arc and the real axis. O, observed points; ◕, calculated points; numbers beside data points refer to the measuring frequency in Hz

Table 2. Distribution parameters of relaxation times for propylene glycol oligomers, PPG and PPGA

Distribution parameter β of the Davidson-Cole Equation

Temperature/°C	Monomer[a])	Dimer	Trimer	Tetramer	Pentamer
−20.0	—	0.67	—	—	—
−30.0	—	0.62	—	—	—
−40.0	—	0.59	—	—	0.49
−45.0	0.663(−45.4 °C)	—	—	0.45	0.46
−50.0	—	0.55	0.55	0.46	0.51
−55.0	0.664(−55.4 °C)	—	0.49	0.51	0.50
−60.0	—	0.53	0.53	0.52	—
−65.0	0.666(−65.5 °C)	—	0.50	—	—

Distribution parameters $1-\alpha$ and β of the Havriliak-Negami Equation [10]

Temperature/ °C	PPG		PPGA	
	$1-\alpha$	β	$1-\alpha$	β
−44.8	0.923	0.433	0.875	0.493
−48.7	0.945	0.421	0.901	0.470
−55.0	0.928	0.433	0.892	0.454

[a]) Davidson DW, Cole RH (1951) J Chem Phys 19:1484

is not observed for pentapropylene glycol because the dielectric strength for the pentamer is seemingly too small to be measured by the bridge.

It is thus concluded that the distribution of relaxation times depends on hydrogen-bonded cluster for the short glycols from monomer to tetramer, but becomes independent of chain length for the glycols longer than tetramer where the effect of hydrogen bonding is rather weak.

Variation of relaxation times with the degree of polymerization of the glycols

Measurement of dielectric relaxation times of propylene glycol oligomers is carried out with the inten-

tion of comparing them with those of ethylene glycol oligomers, because it is interesting to investigate the different relaxational behaviors of very similar molecules such as these two glycols. Koizumi reported the dielectric relaxations of ethylene glycol oligomers by high frequency measurement [12].

Figure 6 shows the comparison of the dielectric relaxation times of ethylene glycol oligomers with those of propylene glycol oligomers.

Similar tendencies are found in these two curves as follows:

1) Both monomers show the shortest relaxation times of the oligomers observed.

2) In contrast to the short dielectric relaxation times of the monomers, those of the dimers are the longest of all.

3) The relaxation times thus change in a zigzag manner with increasing chain length.

It is interesting that the relaxation times of the larger homologous glycols studied are shorter than those of the dimers. It is concluded from the same tendency in Figure 6 for two glycols that the difference of molecular structure concerning methyl group between the two homologues does not affect their relaxational behaviors. If the relaxational mechanism changes from molecular rotation to segmental motion between the dimer and the trimer, remarkable widening of distri-

bution of relaxation times should occur with this change in the mechanism.

Relationship between the relaxation times and the viscosities of the two glycols

It is necessary to analyze the relaxational behaviors shown in Figure 6 in terms of appropriate factors determining these dielectric relaxations. For example, the relaxation time τ is related to the internal friction coefficient ξ by the Equation [18]:

$$\tau = \frac{\xi}{2\,kT} \qquad (3)$$

In the case of spherical or nearly spherical molecules, Stokes law can be used to relate the internal friction coefficient ξ with the molecular radius a and the viscosity η:

$$\xi = 8\pi\eta a^3 \qquad (4)$$

Empirically we can be sure that the dielectric relaxation time in a liquid state is related to the molecular volume and the viscosity of the medium. The latter is determined mainly by intermolecular hydrogen bonding for these liquid glycols. Explanation of the chain length dependences of relaxation times in Figure 6 is discussed from this viewpoint.

Figure 7 shows the viscosities of the glycols vs. reciprocals of absolute temperatures. The effects of the OH...O hydrogen bonding on the viscosities are seen in this figure since the glycols having OH end groups show clearly larger viscosities than the glycols having CH_3COO end groups. These temperature dependence curves show the larger gradients and curvatures for the glycols having the larger hydrogen bonding effects.

Figure 8 shows the comparison of degree of polymerization dependences of the viscosities and those of the dielectric relaxation times of the two homologues. As for propylene glycol oligomers, the viscosities and the dielectric relaxation times of the dimer are larger than those for the monomer and the trimer. In the case of ethylene glycol oligomers, however, the viscosities increase continuously with the increasing chain length as is seen in Figure 8. The reason for such disagreement between the relaxational and the viscous phenomena is difficult to understand because agreement between the two behaviors associated with rotational diffusion has been often reported.
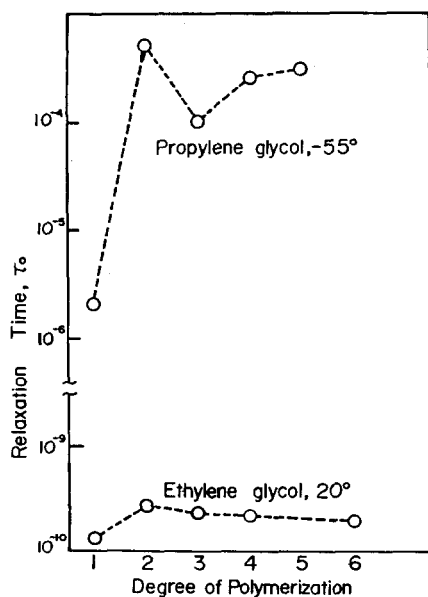

Fig. 6. Relaxation times vs. degree of polymerization for propylene glycols [monopropylene glycol (Ref. [14]), dipropylene glycol (Ref. [8]) and for ethylene glycols (Ref. [10])
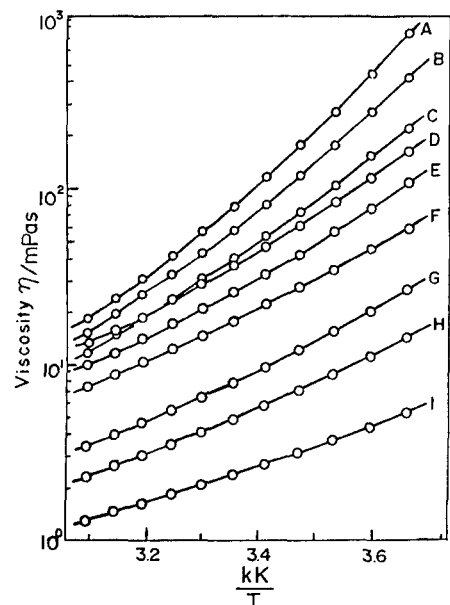
Fig. 7. Viscosities vs. reciprocal absolute temperatures for ethylene, propylene glycol and propylene glycol diacetate oligomers: A, dipropylene glycol; B, tripropylene glycol; C, monopropylene glycol; D, triethylene glycol; E, diethylene glycol; F, monoethylene glycol; G, tripropylene glycol diacetate; H, dipropylene glycol diacetate; I, monopropylene glycol diacetate
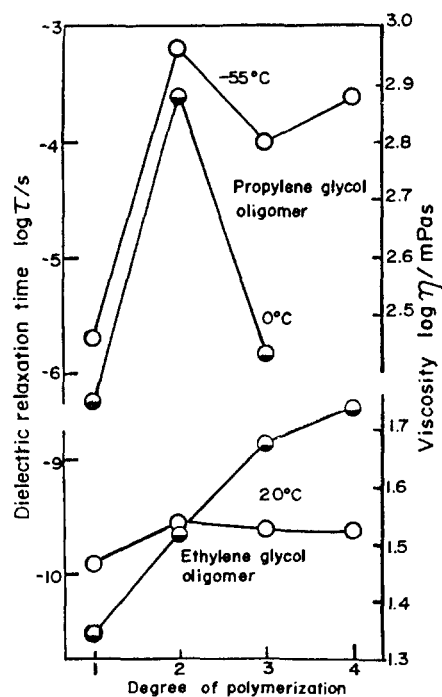

Fig. 8. Viscosities η and dielectric relaxation times τ against the degree of polymerization of the oligomer: O, dielectric relaxation times; ◓, viscosity
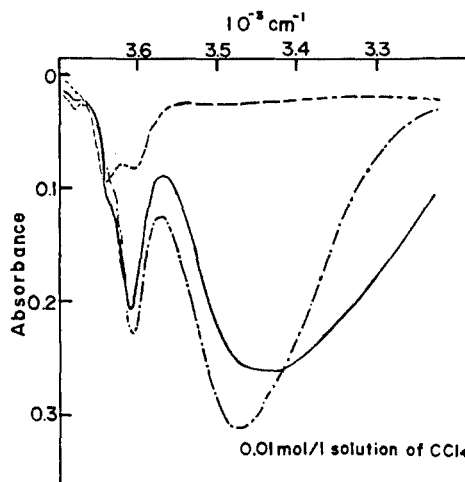

Fig. 9. Comparison of the OH spectra of the three different ethylene glycol oligomers: — — — —, monoethylene glycol; ————, diethylene glycol; —·—·—, triethylene glycol
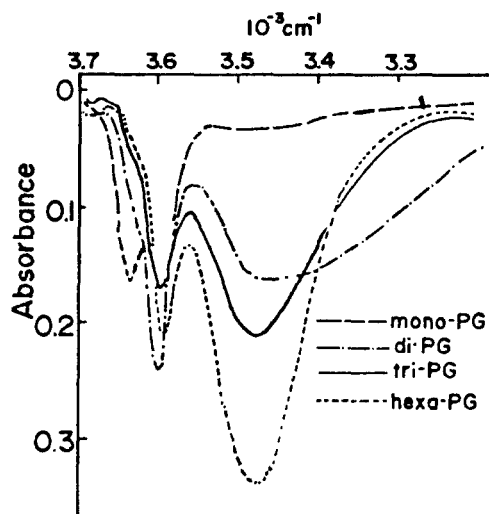

Fig. 10. Variation of the OH stretching vibration spectra with degree of polymerization of propylene glycol oligomers in 0.01 mol/l carbon tetrachloride

Effects of hydrogen bond on the relaxational behavior

The infrared spectra of the two glycols in solution were observed to clarify why the relaxation times and the viscosities of the dimers are largest, with the exception of the viscous behavior of ethylene glycol oligomers. Figures 9 and 10 show the infrared spectra of carbon tetrachloride solution of the two glycols. Only the spectra of OH stretching vibration region were studied because the hydrogen bond effects observed in the OH

Table 3. Wave numbers (cm^{-1}) of various OH stretching vibrations measured in 0.01 mol/l solution of carbon tetrachloride

Sample	Types of hydrogen bond				
	Free OH	Semi-free OH	Intra OH	Inter(I) OH	Inter(II) OH
Monopropylene glycol	3650	3635	3595	—	—
Dipropylene glylcol	—	3630	3600	3475	3340
Tripropylene glycol	—	3630	3595	3475	3340
Hexapropylene glycol	—	3630	3590	3475	—
Monoethylene glycol	3650	3640	3605	—	—
Diethylene glycol	—	3630	3610	3485	3380
Triethylene glycol	—	3630	3610	3475	3380
1,8-octamethylene Glycol	3650	3630	3590	3450	—

because the hydrogen bond effects observed in the OH frequency shifts are remarkable in this region. Many absorption peaks due to OH stretching vibration observed as is seen in Figures 9 and 10 exhibit superposion of the absorption peaks of the different types of OH ... O bonds. Intermolecularly and intramolecularly hydrogen-bonded stretching vibrations are observed between 3600 and 3340 cm^{-1}. Each peak was separated by a curve resolver and identified to reasonable modes, as is shown in Table 3. It is found from the analysis of these spectra that the relative intensity of intramolecularly hydrogen-bonded OH absorption of the dimers is larger than those for the other oligomers [19]. From these results, it is concluded that the molecular structures of the dimers take intramolecularly hydrogen-bonded ring form as well as the trimers as is shown in Figure 11. This molecular structure is also confirmed by the thermodynamic data of the glycols. Several thermodynamic parameters of these glycols are tabulated in Table 4 to ascertain this conclusion though the data are not ample. Above all, the Trouton constant, entropy change between the liquid and the gas phases, of diethylene glycol is the smallest. This result leads to the conclusion that cluster formation by intermolecular hydrogen bond is less than that for the other ethylene glycols.
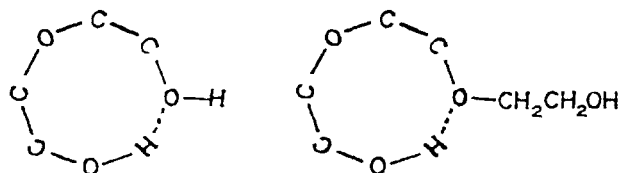

Fig. 11. Hydrogen-bonded ring structure of the dimer and the trimer

Figure 12 compares the dielectric absorption curve of PPG with that of PPGA to find the effects of hydrogen bond on the distribution of relaxation times. A numerical comparison of distribution parameters of PPG with those of PPGA is made in Table 2. These results explain that the distribution of relaxation times

Table 4. Comparison of the thermodynamic properties of ethylene glycol oligomers with those of propylene glycol oligomers

Degree of polymerization	Melting points/°C		Boiling points/°C	
	Ethylene glycol	Propylene glycol	Ethylene glycol	Propylene glycol
Monomer	−12[a]	−60[c]	197.5[c]	187.3[c]
Dimer	− 6[a]	glassy	245.5[c]	231.9[c]
Trimer	− 8[a]	glassy	288[c]	—
Tetramer	− 3[a]	glassy	—	—
Pentamer	− 8.7[d]	glassy	—	—
Hexamer	5− 7[a]	glassy	—	—
Heptamer	7.7[d]	glassy	—	—

Degree of polymerization	Heat of vaporization/kcal mol^{-1}		Trouton constant /cal mol^{-1} K^{-1}	
	Ethylene glycol	Propylene glycol	Ethylene glycol	Propylene glycol
Monomer	12.49[c]	12.48[c]	28.98[d]	27.11[c]
Dimer	13.83[c]	12.89[c]	24.14[d]	
Trimer	17.35[c]		30.95[d]	
Tetramer	21.3[d]		36.66[d]	

[a]) Koizumi N, Hanai T (1956) J Phys Chem 60:1496; [b]) Curme Jr GO, Johnston F (1952) Glycol, Reinhold, New York, Chap 1, 3, and 7; [c]) Union Carbide Chemicals Co. Catalog, Glycols; [d]) Gallaugher AF, Hibbert H (1937) J Amer Chem Soc 59:2514; [e]) Riddick JA, Bunger WB (1970) Organic Solvents, Wiley-Interscience, New York, Chap. III
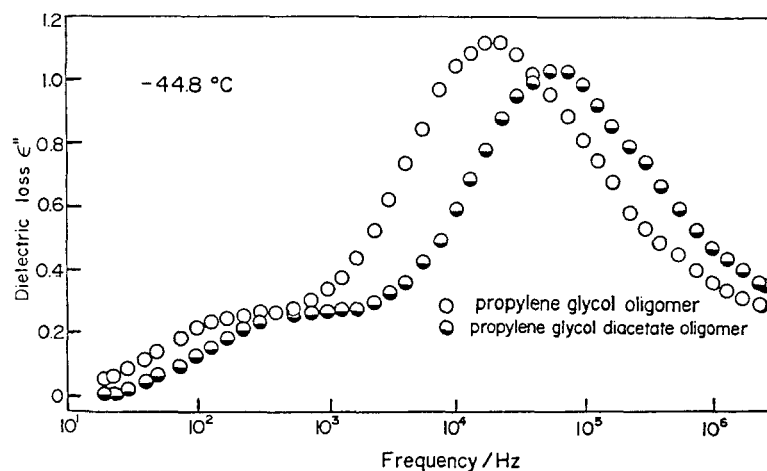
Fig. 12. Comparison of the dielectric loss curve of PPG with that of PPGA at the same temperature

of such long-chain glycols almost does not depend on hydrogen bond but the relaxation times are clearly governed by breaking and reforming of hydrogen bond.

Conclusion

1. The dielectric relaxation times and the viscosities of these glycols change markedly with the degree of polymerization smaller than 10, but the distribution of relaxation times does not change as much as the relaxation times do.

2. In the molecular weight region studied, the dielectric relaxation times cannot be related directly with their degree of polymerization. The inter- and intramolecular hydrogen bond OH . . . O between the chain ends plays an important role in the dielectric relaxation times.

3. It is difficult to ascertain definitely any clear change showing transformation of the relaxational mechanism such as molecular rotation to segmental motion, but this translation appears to occur between the dimer and the trimer because the relaxation times of the trimer are smaller than those of the dimer, despite the marked increase of chain length from the dimer to the trimer.

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