Dielectric, mechanical and thermal properties of some chlorinated poly (*p*-phenylene oxide)s in the solid state

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The dielectric, mechanical and thermal properties were investigated for poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO), poly(2-chloro-6-methyl-1,4-phenylene oxide) (PCMPO) and poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO). PDCPO exhibited two dielectric secondary relaxations designated as β and γ processes around 160 and 100K, respectively. The γ process was assigned to the motion of a trace of chloroform included in the PDCPO film. A blend film PDMPO/PCMPO (9/1 mixing ratio) exhibited dielectric relaxation around 330K and the process was assigned to the rotation of phenyl group with respect to oxygen–phenyl–oxygen axis. No dielectric relaxation was observed for the PDMPO film dried carefully, while the PDMPO film kept under an atmosphere of water vapour exhibited dielectric relaxation due to the motion of the water molecules at about 180K. Tensile stress at break measured on PDCPO prepared by Stamatoff's method was 38 MPa and was much higher than that for PDCPO prepared by the method reported by Blanchard *et al.* Temperature dependence of the dynamic Young's modulus for PDCPO measured at 110 Hz exhibited no appreciable loss peak in the range below 480K. Glass transition temperatures for PDCPO, PCMPO and PDMPO were determined to be 490, 445 and 500K, respectively, by differential scanning calorimetry.

(Keywords: Poly(2,6-dichloro-1,4-phenylene oxide); poly(2-chloro-6-methyl-1,4-phenylene oxide); poly(2,6-dimethyl-1,4-phenylene oxide); dielectric relaxation; mechanical relaxation; glass transition)

INTRODUCTION

Derivatives of poly(*p*-phenylene oxide) (PPO) are known as a group of thermally stable polymers[1]. Because of this practical importance, the physical properties of these derivatives, especially those of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMO), have been investigated by many authors during last two decades[2-14]. However, few studies were carried out on the physical properties of halogenated poly(*p*-phenylene oxide), which is known to have an excellent fire-retardant property[15]. In the present study, the dielectric, mechanical and thermal properties have been investigated for poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO), poly(2-chloro-6-methyl-1,4-phenylene oxide) (PCMPO) and PDMPO.

It was reported that derivatives of poly(*p*-phenylene oxide) exhibit a variety of mechanical and dielectric secondary relaxation processes[2-13]. The data for PDMPO reported by many authors[2-9,11,12] indicated that PDMPO exhibits at least four mechanical relaxations at about 300, 200, 150 and 90K. Yee[11] attributed the processes at 300 and 90K to rotation of phenyl and methyl groups, respectively. Data of dielectric measurement[6,7] on PDMPO indicated only one secondary relaxation at about 180K. For halogenated poly(*p*-phenylene oxide), de Petris[13] reported that PCMPO exhibits two mechanical relaxations at 400 and 150K at 7 kHz. However, no mechanical and dielectric data have been reported for PDCPO.

Comparing the molecular structures of the three poly(*p*-phenylene oxide) samples employed in this study, we note that PDMPO and PDCPO do not have a component of dipole moment in the direction perpendicular to the oxygen–phenyl–oxygen axis, while PCMPO has such a component. Therefore, if there exists a mode of molecular motion associated with rotation of phenyl group, only PCMPO is expected to exhibit dielectric relaxation. On the other hand, a mode associated with the motion of ether groups will give rise to dielectric relaxation in all the samples. The primary objective of this study is to investigate the mechanism of secondary relaxations in PDCPO, PCMPO and PDMPO by comparing their relaxation behaviour.

Two methods for preparing high molecular weight PDCPO were reported by Blanchard *et al.*[16] and by Stamatoff[17]. Although the molecular structure of PDCPO is similar to that of PDMPO, the mechanical properties of PDCPO prepared by the former method are known to be extremely poor[18]. Harrod *et al.*[18,19] concluded that the reason for this poor mechanical property is the highly branched structure in the PDCPO. On the other hand, Stamatoff reported that his method gave linear PDCPO[17]. In order to clarify the effect of branching on the mechanical and dielectric properties, measurements have been made on the PDCPO samples prepared by two methods.

In our previous study[20], it was found that water included in hydrophobic polymers causes dielectric re-

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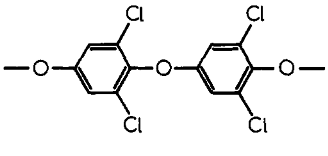
laxation around 200K. For PDMPO, several authors[4,7,9] pointed out that the relaxation around 150K is due to 'water relaxation'. In order to examine the effect of water and diluents on the dielectric properties of poly(*p*-phenylene oxide)s, measurements have also been made on samples including water and chloroform.

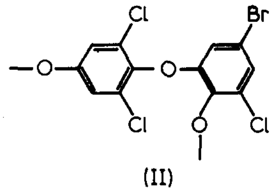
EXPERIMENTAL

Materials

The samples of PDMPO and PCMPO were prepared from 2,6-dimethylphenol and 2-chloro-6-methylphenol, respectively, according to the procedure described by Hay[21] by using a pyridine/nitrobenzene mixed solvent (1/3 ratio) and $CuCl_2$ catalyst. PDCPO was prepared by two methods reported by Blanchard *et al.*[16] and by Stamatoff[17]. We designate the PDCPO prepared by the former method as PDCPO(B) and the latter as PDCPO(S). PDCPO(B) was prepared by decomposition of a complex composed of copper, pyridine and 2,4,6-trichlorophenol in benzene at 70°C. On the other hand, PDCPO(S) was prepared from sodium 4-bromo-2,6-dichlorophenol. The procedure of preparation and characterization of PDCPO(S) were described elsewhere[22]. Molecular weights were determined by gel permeation chromatography (g.p.c.) with an instrument equipped with a low-angle laser light scattering detector (Toyo Soda HLC-801 A)[23,24]. The results are listed in *Table 1*.

The polymerization reaction for PDCPO proceeds normally at the *para*-position (formula I), but irregular reaction occurs at the *ortho*-position as indicated by formula II:


(I)


(II)

The content of the monomeric unit which was incorporated by *ortho*-linkage in PDCPO(S) was determined to be 2 to 3% by chemical analysis of residual Br. The ^{13}C n.m.r. spectrum[22] for PDCPO(S) indicated that a small number of irregular linkages exist in the PDCPO molecule, while the spectrum for PDCPO(B) exhibits a very complicated pattern due to a large number of irregular linkages.

Film preparation

The films of PDCPO(S) and PDMPO were cast from benzene and chloroform solutions, respectively. Unfortunately the films of PCMPO and PDCPO(B) were so brittle that they broke easily when being held with tweezers. Therefore, measurements were performed on a blend PDMPO/PCMPO (90/10) and on a blend PDCPO(B)/PDCPO(S) (26/74). The film of the former system was cast from a benzene solution, and the latter from a chloroform solution. Both blend films were transparent but miscibility of these polymers was not examined. The cast films were dried at 390K in vacuum of 1 Pa for 20 h and further at 430K for 1 h. For dielectric measurement, the films were coated with gold by evaporation.

Table 1 Molecular weight for PDCPO(S), PDCPO(B), PCMPO and PDMPO

Sample	$10^{-3} M_w$
PDCPO(S)	390
PDCPO(B)	26
PCMPO	10
PDMPO	330

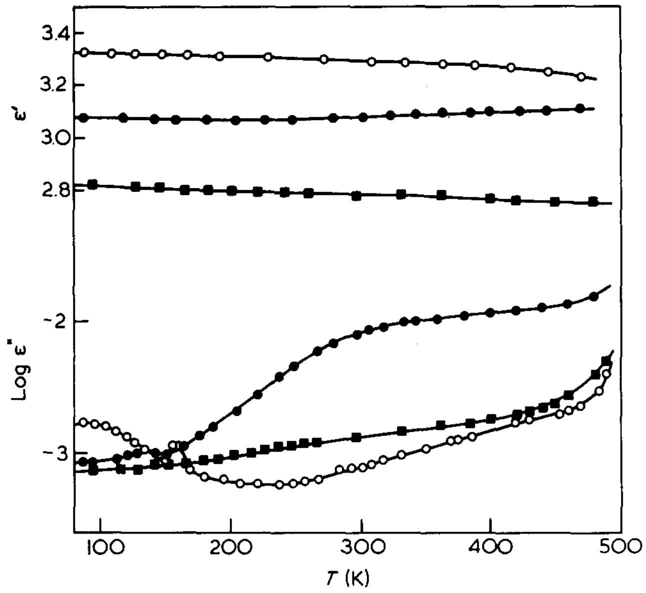


Figure 1 Comparison of the temperature dependence of ε' and log ε" at 1 kHz for PDCPO(S) (○), PDMPO (■), and the PDMPO/PCMPO (1/9) blend (●)

In order to examine the effect of water and chloroform on the dielectric properties of PDMPO and PDCPO, the sample films were doped with water and chloroform by placing the films coated with gold in an atmosphere of water or chloroform vapour for several hours at 298K. From weight increment, the content of water and chloroform in the polymer was determined to be 1.4 and 30 mg g^{-1}, respectively.

Method

Dielectric measurement was carried out with a capacitance bridge (General Radio 1615-A) at 0.1, 1 and 10 kHz over a temperature range from 80 to 500K. Except for the films doped with water or chloroform, the sample film was dried again in vacuum of 10^{-1} Pa at room temperature for 12 h after the film had been set in a capacitance cell. After this drying procedure, the cell was filled with helium gas. Dynamic Young's modulus and tensile strength were measured on Rheovibron (Toyo-Baldwin, DDV II-C) and on a tensile tester (Iwamoto Co.), respectively. The differential scanning calorimeter (Rigaku Denki, Type-YDS) was used at heating rate of 10K min^{-1}.

RESULTS AND DISCUSSION

Comparison of dielectric behaviour between PDCPO(S), PDMPO and PCMPO/PDMPO

Temperature dependence of dielectric constant ε' and loss factor ε" at 1 kHz for PDCPO(S), PDMPO and PCMPO/PDMPO blend are shown in *Figure 1*. For PDCPO(S), a weak relatively sharp loss peak and a broad loss peak were observed at 160 and 90K, respectively, and were designated as β and γ processes, respectively. On the other hand, PCMPO/PDMPO exhibited a very broad (β) peak around 330K and a small (γ) peak at about 120K. In contrast, PDMPO did not exhibit a loss peak over the wide temperature range from 80 to 450K. Comparison between the loss curves of PDMPO and the PCMPO/PDMPO blend indicates that the relaxations observed for the PCMPO/PDMPO blend are associated with the motion of the PCMPO molecule. The activation energies and temperatures of loss maximum at 1 kHz for these relaxation processes are listed in *Table 2*. For the three samples, increase of ε'' was seen around 500K, indicating the onset of primary (α) relaxation process[5,13]. In contrast to the complicated change in ε'', the values of ε' for the three samples are almost independent of temperature. From *Figure 1*, we note that behaviour of the secondary relaxations for the three samples differs greatly from each other in spite of their similarity in structure.

There are four possible origins responsible for these secondary relaxations. First, local twisting motion of the ether group as proposed by Yamafuji and Ishida[25] is expected to cause a local mode process. Secondly, rotation of the phenyl group with respect to the oxygen–phenyl–oxygen axis may be considered. Obviously, this mode is inactive for PDMPO and PDCPO. Thirdly, the motion of the monomeric unit with *ortho*-linkage or the motion of short chain branch is expected as the origin: we call this process defect mode. Fourthly, motion of simple molecules such as water and chloroform occluded in the polymer matrix may cause dielectric secondary relaxation[7,20].

To summarize we can expect (i) the motion of the ether group, (ii) phenyl rotation, (iii) defect mode and (iv) the motion of simple molecules. In the following sections, we discuss the mechanism of the relaxations observed for each sample of PPO derivatives on the basis of the possibilities mentioned above.

Dielectric relaxations in PDCPO and PDMPO

As shown above, PDMPO does not exhibit dielectric secondary relaxation. This indicates that motion of the ether group does not occur in PDMPO and suggests that the β and γ processes of PDCPO are not due to the first mechanism mentioned above. Since the second mechanism is not applicable to PDCPO, the relaxations in PDCPO may be attributed to either the third or the fourth mechanism. In order to examine whether the dielectric relaxations in PDCPO are due to the fourth mechanism, measurements were carried out on a PDCPO(S) which was allowed to stand in an atmosphere of chloroform and water vapour. The results are shown in *Figures 2* and *3*. Measurement was also made on PDCPO(B)/PDCPO(S) blend in order to check the third possibility (*Figure 2*).

As shown in *Figure 2*, the γ peak was enhanced remarkably by doping with chloroform (3.0% by weight). Therefore, the γ process can be attributed to the motion of the chloroform molecules. In spite of drying at 430K, the casting solvent, chloroform, remained slightly in the film.

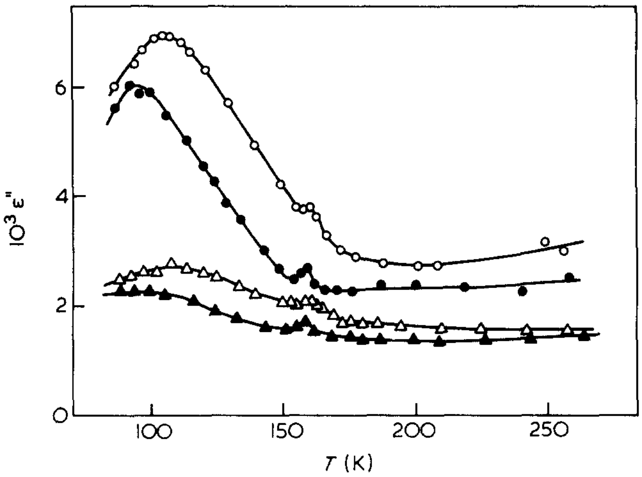


Figure 2 Temperature dependence of ε'' for the PDCPO(S) film doped with chloroform (3.0 wt%) (●, 1 kHz; ○, 10 kHz) and that for the PDCPO(B)/PDCPO(S) blend (26/74) (▲, 1 kHz; △, 10 kHz)

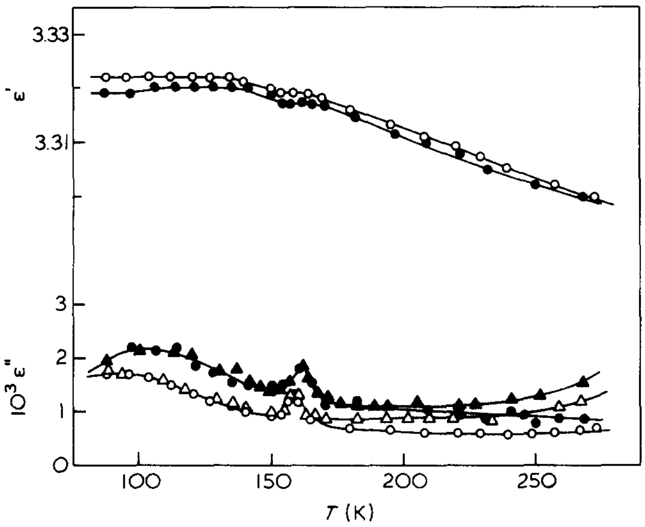


Figure 3 Temperature dependence of ε' and ε'' for PDCPO(S) dried in vacuum (○, 1 kHz; ●, 10 kHz) and those for PDCPO(S) allowed to stand in moisture (△, 1 kHz; ▲, 10 kHz)

Table 2 Activation energy, E_a, temperature of dielectric loss maximum at 1 kHz, T_{max}, the mechanism of the relaxation process, and glass transition temperature, T_g

Sample	Designation of process	E_a (kJ mol^{-1})	T_{max} (K)	Mechanism of the process	T_g (K)
PDCPO(S)	β	134	160		490
	γ	17.3	95	Motion of $CHCl_3$	
PCMPO/PDMPO	β	86	330	Phenyl rot.	
(10/90)	γ	26.4	115		
PCMPO					445
PDMPO (wet)		48	180	Motion of H_2O	500

The magnitude of dielectric relaxation $\Delta\varepsilon$ for this process was determined from the area of the loss peak under the ε'' *versus* T^{-1} curve by using the relation[26]:

$$\Delta\varepsilon_{\mathrm{obs}}=(2E_a/\pi R)\int\varepsilon''\,\mathrm{d}(1/T) \qquad (1)$$

where E_a denotes activation energy (17 kJ mol^{-1}). The calculation for the ε'' curve at 10 kHz resulted in $\Delta\varepsilon_{\mathrm{obs}}=0.036\pm0.01$. This value was compared with the theoretical magnitude of dispersion given by[26]:

$$\Delta\varepsilon_{\mathrm{calc}}=\frac{4\pi N\mu^2\varepsilon_0(\varepsilon_\infty+2)^2}{9kT(2\varepsilon_0+\varepsilon_\infty)} \qquad (2)$$

where N denotes the number of dipoles with moment μ in unit volume, and ε_0 and ε_∞ are static and high-frequency dielectric constant, respectively. From the content of chloroform in PDCPO, N was calculated by using the density (1.557 g ml^{-1}) at 298K. For the dipole moment of chloroform, 1.02 D was employed[27] ($1\ \mathrm{D}=3.336\times10^{-30}$ C m). Thus $\Delta\varepsilon_{\mathrm{calc}}$ has been calculated to be 0.20. The value of the observed magnitude of dispersion is about 1/6 of $\Delta\varepsilon_{\mathrm{calc}}$, indicating restricted motion of the chloroform molecules in the PDCPO matrix.

For the mechanism of the β process of PDCPO, the defect mode would be expected as the possible origin. As mentioned in the experimental section, the content of irregular linkages in PDCPO(B) is much higher than that in PDCPO(S). Therefore, if the defect mode is the origin of the process, the loss peak for the PDCPO(B)/PDCPO(S) blend should be higher than that for PDCPO(S). However, as shown in *Figure 2*, the amplitudes of the β peaks for both samples are nearly the same, and hence the possibility of the third mechanism can be ruled out. At present, we cannot assign the mechanism of the β process. We note that the behaviour of this relaxation process is unusual compared with ordinary secondary relaxation processes: the loss peak is very sharp and the activation energy (134 ± 10 kJ mol^{-1}) is higher than those for other polymers.

Figures 3 and *4* indicate, respectively, the temperature dependence of ε' and ε'' for PDCPO(S) and PDMPO measured after they were kept in an atmosphere of water vapour over a saturated aqueous solution of $CoCl_2$ at 298K. The content of water in PDMPO was determined to be 0.14% by weight, while that in PDCPO was less than 0.01%. As shown in *Figures 3* and *4*, PDMPO exhibits clear 'water relaxation' at about 180K but PDCPO does not. Even the PDCPO film kept in a water atmosphere for 60 days at room temperature (20° to 30°C) did not absorb an appreciable amount of water. The PDCPO(S) film exposed to moisture exhibited slightly larger ε'' than the dry film at 270K. This increment in ε'' may be attributable to proton conduction due to a very small amount of water included in the film.

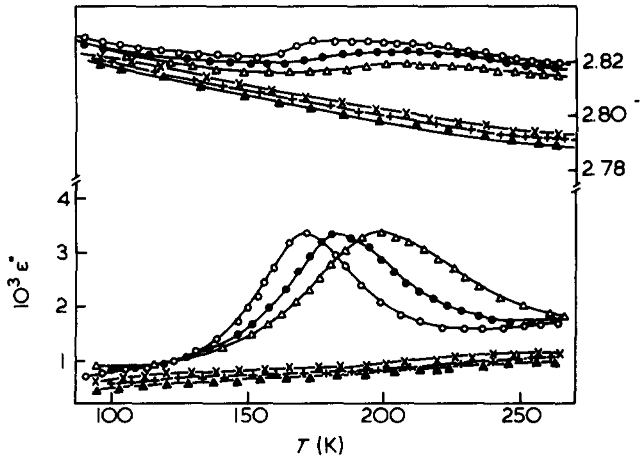


Figure 4 Temperature dependence of ε' and ε'' for PDMPO dried (x, 100 Hz; +, 1 kHz; ▲, 10 kHz) and those for PDMPO including 0.14% water (○, 100 Hz; ●, 1 kHz; △, 10 kHz)

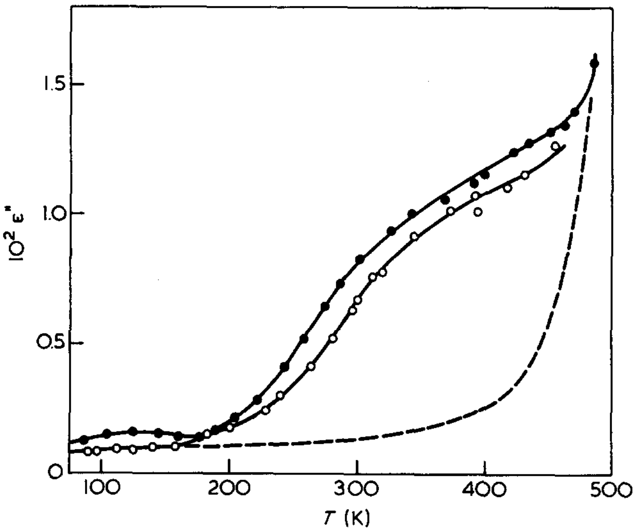


Figure 5 Temperature dependence of ε'' for the PDMPO/PCMPO (10/90) blend (●, 1 kHz; ○, 10 kHz). The broken curve indicates the baseline estimated to calculate the magnitude of dispersion

In the previous paper[20], we concluded that, with the increase in polarity of polymer matrices, the amplitude of the water relaxation peak increases. Since the C–Cl bond moment is greater than that for C–CH_3 bond, the present result contradicts the tendency observed previously. We note that dipole moment is not an essential factor in determining the content of water in polymers. From the above result, it can be expected that the PDCPO film is practically useful as a 'water barrier film'.

Karasz *et al.*[6] reported that PDMPO dried in vacuum at 470K for 12 h exhibited a dielectric loss peak around 180K. This contradicts the result reported by Allen *et al.*[7] who attributed this relaxation to motion of the water molecules. The present results shown in *Figure 4* support the conclusion by Allen *et al.* Based on equations (1) and (2), the values of $\Delta\varepsilon_{\mathrm{obs}}$ and $\Delta\varepsilon_{\mathrm{calc}}$ for the 'water relaxation process' were calculated to be 0.020 and 0.066, respectively. The ratio of $\Delta\varepsilon_{\mathrm{obs}}$ and $\Delta\varepsilon_{\mathrm{calc}}$ is 0.33, in fairly good agreement with the ratio observed for various hydrophobic polymers[19]. This result suggests that free rotation of water molecules is restricted in PDMPO.

Dielectric relaxation in PCMPO

The PCMPO/PCMPO blend exhibits a loss peak (β) around 330K. Since the amplitude of this process is relatively high, the process may be attributed to the rotation of phenyl groups in the PCMPO molecules. In order to confirm this possibility, we again compared the values of $\Delta\varepsilon_{\mathrm{obs}}$ and $\Delta\varepsilon_{\mathrm{calc}}$ for this process. The results of the calculation are $\Delta\varepsilon_{\mathrm{obs}}=0.14$ and $\Delta\varepsilon_{\mathrm{calc}}=0.10$. For the evaluation of $\Delta\varepsilon_{\mathrm{obs}}$, we assumed that the baseline of the loss curve is given by the broken curve shown in *Figure 5*.

The dipole moment associated with the rotation of the monomer unit of PCMPO was calculated to be 1.70 D from the bond moment for C–Cl (−1.59 D) and that for C–CH_3 (+0.37 D)[28]. Fairly good agreement between $\Delta\varepsilon_{obs}$ and $\Delta\varepsilon_{calc}$ confirms the mechanism of phenyl rotation for the β process. Yee[11] and de Petris *et al.*[3] attributed the mechanical relaxation observed for PDMPO around 350K to motion of the phenyl group. Their results correspond well to the present result.

The activation energy for the β process in the PCMPO/PDMPO blend was estimated to be 86 kJ mol^{-1} from shift of the loss curve with frequency, because of the broadness of the loss peak. Tonelli[29] calculated the energy barrier for the rotation of the phenyl group to be about 4 kJ mol^{-1} for PDMPO and poly(2,6-diphenyl-1,4-phenylene oxide). The activation energy for rotation of the phenyl group is much higher than the calculated intramolecular energy barrier. Since the phenyl group is bulky, the activation energy in the glassy state arises mainly from intermolecular interactions.

With regard to the γ process, we cannot assign the mechanism of this process. Obviously, this mode is not attributable to the motion of benzene employed for casting.

Mechanical and thermal properties

Figure 6 shows the temperature dependence of dynamic Young's modulus measured at 110 Hz for PDCPO(S). The change in storage modulus E' clearly exhibits the primary relaxation around 500K. For PDMPO it was reported[5,11,12] that four small mechanical relaxations exist below 400K. In the present study the loss modulus E'' for PDCPO exhibited no such relaxations. Comparison of E' for PDCPO and PDMPO indicates that PDCPO has similar mechanical strength to PDMPO[5,11,12].

By measuring tensile stress, it was found that PDCPO(S) exhibited ductile failure. The stress at the yield point and that at break were determined to be 46 and 38 MPa, respectively. These values are similar to those of PDMPO[12]. In contrast to PDCPO(S), the stress at break for PDCPO(B) was so small that no meaningful data were obtained.

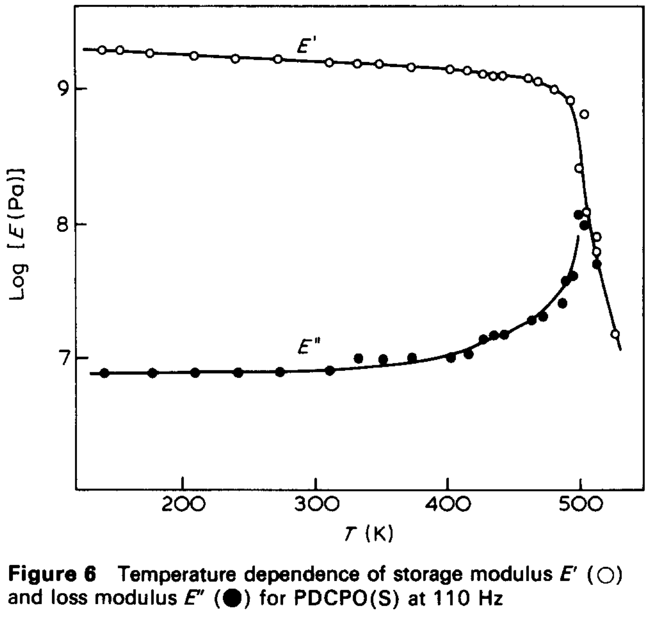


Figure 6 Temperature dependence of storage modulus E' (○) and loss modulus E'' (●) for PDCPO(S) at 110 Hz

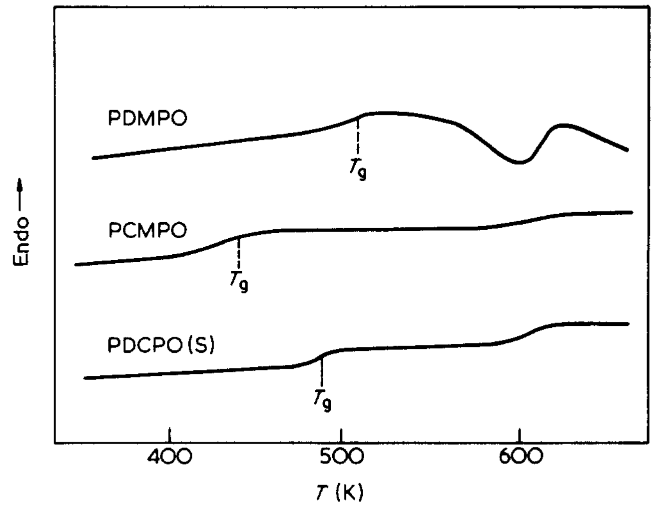


Figure 7 D.s.c. thermograms for PDMPO, PCMPO and PDCPO(S) at a heating rate of 10K min^{-1}

Figure 7 shows the d.s.c. thermograms for PDCPO(S), PCMPO and PDMPO. The steplike change in the thermograms around 500K was attributed to glass transition as listed in *Table 2*. It is noted that T_g for PCMPO is relatively low. The low molecular weight of PCMPO may be one of the origins for its low T_g. It is also noted that PDMPO and PDCPO exhibited thermal anomalies at about 620K. Probably these anomalies are due to decomposition of the polymers.

CONCLUSIONS

The PDCPO, PCMPO and PDMPO samples exhibit dielectric relaxations due to various origins. The characteristics and mechanisms for the relaxation processes are summarized in *Table 2* together with their glass transition temperatures. The comparison of the mechanical properties of PDCPO and PDMPO indicates that PDCPO(S) has similar mechanical properties to PDMPO but the mechanical strength of PDCPO(B) is much lower than that of PDMPO.

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