EFFECT OF BROMINATION ON THE THERMAL PROPERTIES OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

R. C. Bopp[1,2], U. Gaur[1,3], R. P. Kambour[2] and B. Wunderlich[1]

Department of Chemistry [1]*Rensselaer Polytechnic Institute Troy, NY 12181;*
Polymer Physics and Engineering Branch [2]*Corporate Research and Development General Electric Company Schenectady, NY 12301, USA*
[3] *Present Address; Personal Products Company, Division of Johnson and Johnson, Inc., Milltown, NJ 08850, USA*

The thermal behavior of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO[K] resin), poly(3-bromo-2,6-dimethyl-1,4-phenylene oxide), and a series of their statistical copolymers with identical average molecular lengths has been characterized by thermogravimetry and computer-interfaced differential scanning calorimetry. The heat capacities are found to be additive with respect to the concentrations of the two components. The change in heat capacity at the glass transition (ΔC_p) is independent of composition for bromination of up to 75 % of the repeat units. At higher bromine levels ΔC_p decreases abruptly. This behavior is attributed to the temperature dependence of ΔC_p for the two components. The glass transition temperature (T_g) of the copolymers varies nearly linearly with composition. A comparison of the experimental values of T_g is made with various equations derived for statistical copolymers and homogeneous polymer blends. A modification of the Couchman equation is presented taking into account the temperature dependence of ΔC_p.

Poly(2,6-dimethyl-1,4-phenylene oxide), a poly(xylenyl ether) abbreviated PXE, is a commercially important polymer known to be compatible with polystyrene over the entire composition range [1, 2]. The incorporation of brominated repeating units (e.g., 3-bromo-2,6-dimethyl-1,4-phenylene oxide) into the PXE backbone has been shown to reduce its compatibility with polystyrene [3, 4] and improve flame resistance [5]. In the present paper we describe measurements of the heat capacity from 310 to 590K for a series of random poly(3-bromo-2,6-dimethyl-1,4-phenylene oxide-*co*-2,6-dimethyl-1,4-phenylene oxide)s, designated PBr$_{\bar{x}}$XE, where $\bar{x}$ is the average mole fraction brominated units.

PBr$_{\bar{x}}$XE copolymers have been obtained by copolymerizing 3,4-dibromo-2,6-dimethyl phenol with 2,6-dimethyl phenol via an oxidative coupling reaction, but this method results in block copolymers due to much faster reaction rates between like monomers rather than unlike monomers [6]. An alternate route to PBr$_{\bar{x}}$XE copolymers involving the direct bromination of the PXE homopolymer is used in this research. The reaction, shown in Figure 1, was first reported by White and Orlando [5].

Bromination of the aromatic ring is specific to the 3-position and proceeds stoichiometrically up to one bromine per ring. Using this procedure several PBrxXE
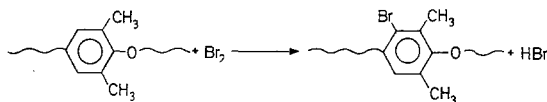
Fig. 1. Bromination of poly(2,6-dimethyl-1,4-phenylene oxide) (PXE)

polymers with $\bar{x}$ varying from 0.25 to 1.0 were synthesized and characterized. The characterization included studies of chain microstructure, phase behavior, and thermal stability. Heat capacity measurements and transition temperature determinations were made by computer-interfaced differential scanning calorimetry (DSC).

Experimental and results

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) ($[\eta]_{25\,°C}^{CHCl_3} = 0.53$ dl/g), supplied by the General Electric Company, Noryl Products Department, Selkirk, NY, was used as the starting material for the synthesis of the $PBr_{\bar{x}}XE$ ($0 < \bar{X} < 1$) copolymers and PBr_1XE homopolymer. The bromination reactions were carried out following a procedure similar to that described by White and Orlando [5]. Stoichiometric amounts of liquid bromine were slowly added to rapidly stirred solutions containing 5 g PXE in 50 ml chloroform to make statistically brominated copolymers designed to contain 0.25, 0.50, 0.75, 0.87, and 0.94 mole fraction brominated repeating units. PBr_1XE homopolymer was prepared in a similar fashion. The brominated polymers were precipitated in 3 to 4 volumes of methanol, filtered, washed with additional methanol, and dried under vacuum for 12−24 hours at 375−400 K. The dried polymers were subsequently redissolved in chloroform (ca. 10 w/v%), cast into films, and dried as before.

Chemical composition

The chemical structure of the brominated polymers was analyzed by proton and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The proton NMR spectra were obtained using a Varian FT-80A spectrometer at 80 MHz. Fourier transform ^{13}C NMR spectra were obtained with Varian FT-80A (20 MHz) and Varian XL-100-15 (25.2 MHz) spectrometers with complete proton decoupling. Deuterated chloroform was used as the solvent, and tetramethylsilane (TMS) served as an internal calibration standard. Also, the samples were doped with 0.1 M tris(acetylacetonato)chromium to shorten T_1's and suppress the Nuclear Overhauser Effect (NOE). Gated decoupling with a 2 s pulse delay was used to insure complete relaxation of all carbon nuclei and to eliminate any residual NOE.

Typical ^{13}C NMR spectra for the PXE and PBr_1XE homopolymers and a copolymer containing 0.75 mole fraction brominated units are shown in Fig. 2. The
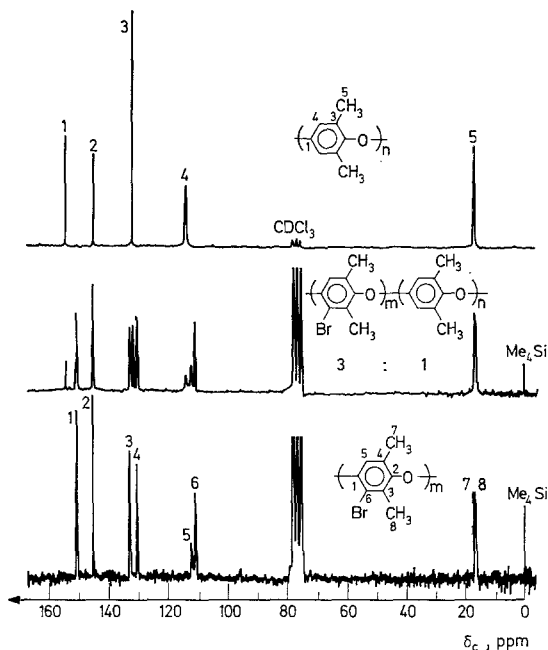
Fig. 2. ^{13}C NMR spectra of PXE and PBr$_1$XE homopolymers and 3 : 1 copolymer (PBr$_{0.75}$XE). Resonance peak numbers correspond to the position of the carbon nuclei as shown in the chemical formulae

peak numbers in the spectra correspond to the carbon nuclei shown in the formulae. From these spectra it is clear that bromination is specific to the 3-position on the aromatic ring and proceeds stoichiometrically. The absence of dibromination was confirmed by comparison of the spectra with that obtained for a copolymer prepared by the oxidative coupling of a 2 : 1 mixture of 3,4,5-tribomo-2,6-dimethyl phenol with 2,6-dimethyl phenol [6, 7]. The mole fractions of brominated units ($\bar{x}$) calculated from the spectra are listed in Table 1 and are in good agreement with the design compositions.

Table 1

Chemical composition determined by ^{1}H and ^{13}C NMR spectroscopy

Sample number	$\bar{x}$, Mole fraction brominated units		
	Stoichiometry	^{1}H NMR	^{12}C NMR
49C	0.25	0.25	0.27
48B	0.50	0.49	0.50
49B	0.75	0.77	0.77
50C	0.87	0.90	0.93
53C	0.94	0.96	0.98
49A	1.00	1.00	1.00

In the case of the copolymer, the resonances for the carbon nuclei in the 1 and 4 positions display multiplicity which can be attributed to the effects of different neighboring rings (brominated or non-brominated). This effect is an indication of the randomness of the bromination reaction.

Molecular weight characterization

Molecular weight determinations were made using viscometry, gel permeation chromatography (GPC), and vapor phase osmometry (VPO). The results for the first two methods are shown in Table 2.

Table 2

Molecular weight characterization
Intrinsic viscosity GPC molecular weights[b], dl/g[b]

| | Intrinsic viscosity | | GPC molecular weights, dl/g | | |
$\bar{x}$[a]	Exp	Calc.	$\overline{M}n$	$\overline{M}w$	$\overline{M}w/\overline{M}n$
0	0.53	—	23,100	38,100	1.65
0.25	0.45	0.46	17,900	62,000	3.50
0.50	0.44	0.40	18,200	59,800	3.28
0.75	0.37	0.35	19.200	60,400	3.14
0.87	0.36	0.34	16,500	59,100	3.59
0.94	0.35	0.33	20,400	70,700	3.47
1.00	0.35	0.32	16,800	57,400	3.41

[a] Mole fraction   brominated repeat units
[b] Solvent: chloroform

Intrinsic viscosity measurements were used to determine whether chain cleavage had occurred during the bromination reaction. Knowing the intrinsic viscosity $[\eta]$ of the PXE starting material, the intrinsic viscosities of the brominated derivatives were calculated from Eq. (1) assuming the chain contour length and the hydrodynamic volume remained unchanged.[8]

$$[\eta] = \Phi \frac{[\langle r^2 \rangle^{3/2}}{M} . \tag{1}$$

In this work M is taken as the molecular weight of an "average repeat unit" in the copolymer and Φ is a composition-independent constant relating the mean square end-to-end distance $\langle r^2 \rangle$ to the intrinsic viscosity. The close agreement between the calculated and experimental intrinsic viscosity values suggests that no significant chain cleavage had occurred during bromination.

GPC measurements were made in chloroform solutions using a Waters Model 244 liquid chromatograph with a R401 refractive index detector. The molecular

weights obtained were calculated using a calibration from polystyrene standards. The results in Table 2 indicate an anomalous molecular weight behavior. Bromination of PXE causes an apparent decrease in $\overline{M}n$ and an increase in $\overline{M}w$, both more or less independent of the degree of bromination. These findings conflict with the viscosity measurements which indicate a continuous increase in molecular weight in accord with the level of bromination.

To resolve this disparity, number average molecular weights of PXE and PBr$_1$XE homopolymers were measured in toluene solution using a Knauer vapor phase osmometer and found to be 11,700 and 15,400, respectively. With the addition of one bromine atom to each repeating unit of PXE of $\overline{M}_n = 11,700$, the molecular weight should increase to 19,400. The VPO results are about 20% lower than expected, but in qualitative agreement with the intrinsic viscosity results, i.e., $\overline{M}n$ increases in proportion to the extent of bromination. The reasons for the probably erroneous GPC results remain unclear.

Solid state characterization

Ultrathin sections of samples covering the whole range of bromine content were analyzed by scanning transmission electron microscopy (STEM) using a JEOL-CO JSEM 200 instrument at magnifications up to 50,000X. No evidence was observed of microphase separation which might have arisen had the bromination not been random. Wide angle X-ray diffraction studies were carried out on a General Electric XRD-4 diffractometer (35 keV/20 ma) using Cu Kα radiation. No indication of crystallinity in any of these samples was found, each exhibiting broad halos typical for amorphous materials.

Densities of cast films of the copolymers were measured in aqueous potassium iodide solutions using the density gradient technique. The density gradient columns were calibrated with glass floats (± 0.0002 gcm^{-3}) supplied by the Scientific Glass Apparatus Company. Densities were found to increase linearly with the extent of bromination as shown in equation (2)

$$\varrho = \varrho° + 0.4201\ \bar{x} \tag{2}$$

where $\varrho°$, the extrapolated density for PXE (1.092 gcm^{-3}), is somewhat higher than the value of 1.063 gcm^{-3} reported by Jacques and Hopfenberg [9]. Equation (2) fits the experimental data with a correlation coefficient of 0.9976.

Thermal analysis

The thermal stability of the PBr$_x$XE polymers was studied using isothermal and non-isothermal thermogravimetry. These data were needed to establish the stability limits for subsequent heat capacity measurements.

Thermogravimetry was performed on a DuPont Thermal Analyzer (Model 990) fitted with a TG Module (Model 951). Isothermal and non-isothermal experiments
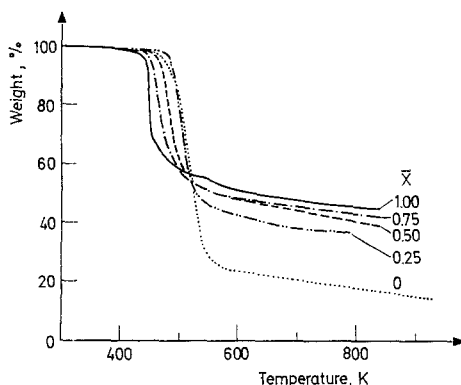
Fig. 3. Non-isothermal thermogravimetry curves for PXE and PBr$_{\bar{x}}$XE polymers in nitrogen. (10 deg min^{-1})

were performed, both, in air and nitrogen. A scanning rate of 10 deg. min^{-1} was used for non-isothermal experiments run from 300 to 1000 K. Isothermal thermogravimetry was performed at 573 K (300°) and the mass loss recorded for 5 — 12 h. For a typical 40 mg sample, the mass accuracy was about $\pm 1\%$. Non-isothermal thermogravimetry curves for PXE and PBr$_{\bar{x}}$XE polymers ($\bar{x}$ = 0.25, 0.50, 0.75 and 1.0) in nitrogen and air are given in Figs 3 and 4, respectively.

In nitrogen, thermal degradation follows a one-step process which is accelerated by the presence of bromine in proportion to its concentration and results in the formation of a black, carbonaceous char. The extent of char formation increases with the degree of bromination. For example, PBr$_1$XE yields about twice the amount of char as found for the unbrominated polymer.

In air, thermal degradation follows a two-step process. The first step is non-oxidative and similar to that found in the nitrogen experiments, being accelerated
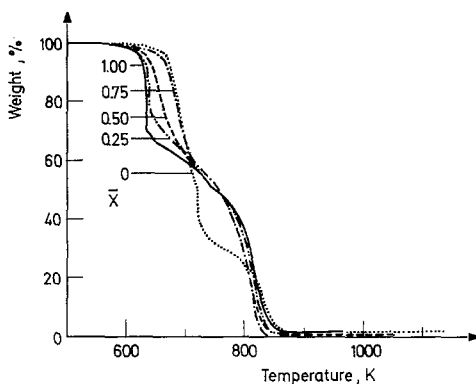

Fig. 4. Non-isothermal thermogravimetry curves for PXE and PBr$_{\bar{x}}$XE polymers in air (10 deg min^{-1})

by the presence of bromine. The second step is an oxidative process which occurs at about 800 K and is unaffected by bromine content. Virtually all the samples had completely volatilized by 850 K.

The temperature of 1% mass loss in these scans is independent of atmosphere and decreases from 623 K for PXE to 595 K for PBr$_1$XE. Accordingly, 590 K was chosen as an upper temperature limit for all samples in subsequent DSC measurements.
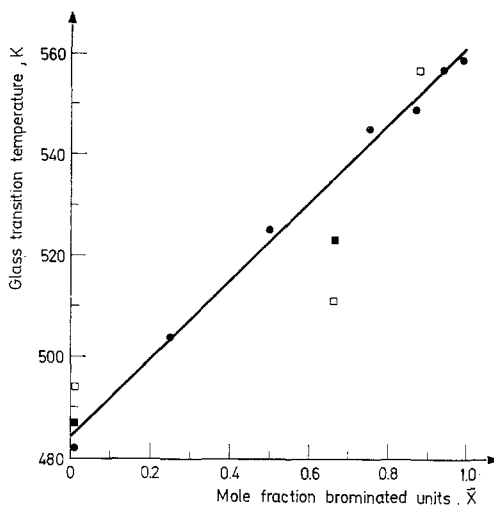

Fig. 5. Glass transition temperatures of PXE and PBr$_{\bar{x}}$XE copolymers. [Filled circles — this work (20 deg min^{-1} heating rate); filled squares — DSC results, Ref. 5 (40 deg min^{-1} heating rate); open squares — TOA results, Ref. 5 (10 deg min^{-1} heating rate); straight line represents Eq. (3)]

Isothermal thermogravimetry at 573 K indicated that PBr$_{\bar{x}}$XE's with $\bar{x} < 0.75$ exhibit less than 1.5% mass loss for periods up to 1 h. Polymers with higher bromination levels exhibited between 5 and 11% mass loss over the same period of time. These findings suggest that scanning calorimetry of copolymers with $\bar{x} > 0.75$ should be terminated at an even lower temperature. From our heat capacity results presented later, this temperature limit was found to be about 550 K.

Preliminary DSC scans were performed on all samples to determine glass transition temperatures (T_g). In each case T_g was taken as the temperature corresponding to half the heat capacity change between the glassy and molten states. The results are given in Table 3 and Fig. 5. T_g varies nearly linearly with composition and is represented by Eq. (3) with a standard deviation of ± 2.2 K.

$$T_g(\mathrm{K}) = 484. + 77.0\,\bar{x} \qquad (3)$$

This behavior is in reasonably close agreement with the empirical copolymer equations of Fox [10] and Wood [11]. Also shown in Fig. 5 are earlier T_g data re-

Table 3

T_g and ΔC_p values

Composition $\bar{x}$[a]	Glass transition temperature, K					ΔC_p, J mol^{-1}K^{-1}
	Exp.	Calculated				
		Wood	Fox	Couchman	Eq. (7)	
0.00	482	482	482	482	482	28.3
0.25	504	504	508	495	502	27.8
0.50	525	523	529	511	520	28.9
0.75	545	542	544	531	538	28.2
0.87	549	551	552	543	548	25.6
0.94	557	555	555	552	554	19.0
1.00	559	559	559	559	559	18.0

[a] Mole fraction brominated repeat units

ported by White and Orlando [5] on PXE and selected PBr$_{\bar{x}}$XE copolymers using DSC (filled squares) and thermooptical analysis (open squares).

To obtain quantitative information on the glass transition, heat capacities were measured for each sample using a computer-interfaced differential scanning calorimeter (Perkin-Elmer DSC2) with an enclosed, air-cooled refrigeration unit (Perkin-Elmer Intracooler II). Continuous transformation of the output amplitudes into digital form was accomplished through an analog-digital converter. The digital output range is $0 - 10,000$, which corresponds to the full scale deflection of the DSC recorder. The data points were sampled every 1.2 s. Calculation of heat capacities from reference measurements (on Al$_2$O$_3$), baseline measurements, and sample measurements were made with a Hewlett-Packard 9821A calculator. The details of equipment, calibration, and programming have been reported earlier [12]. The accuracy of heat capacity is estimated to be better than $\pm 1\%$.

Hermetically-sealed aluminum pans were used for heat capacity measurements. Cast films were cut into discs using a No. 1 cork borer, and $8 - 10$ discs were stacked into each sample pan. The total sample mass was typically $20 - 25$ mg. The samples were introduced into the DSC at 310 K and quickly heated 10 to 20 K above their T_g. After thermal equilibrium had been established (ca. 5 min), the samples were cooled to 300 K at 80 K min^{-1}. The heat capacity was measured from 300 K to temperatures below the start of decomposition in intervals of 20 to 60 K to assure linear variation of the isothermal baseline. A heating rate of 10 deg min^{-1} and a range sensitivity of 21 mJs^{-1} (5 mcals^{-1}) were chosen. The mass of the sample pan was found to remain constant within ± 0.10 mg during heating.

The heat capacities of PXE and the brominated derivatives are shown in Fig. 6. The data points represent average values for three to six measurements which are
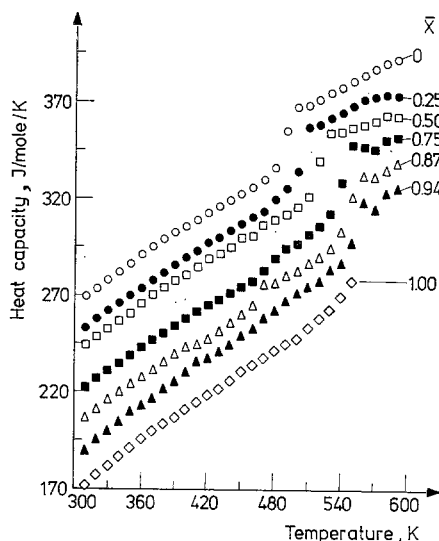
Fig. 6. Heat capacity of PXE and PBr$_{\bar{x}}$XE copolymers. The ordinate corresponds to the PBr$_1$XE sample; all other data are shifted up in intervals of 20 Jmol^{-1}K^{-1})

in agreement within $\pm 1.5\%$. Heat capacity data for all the samples below and above the glass transition were fitted with an inverse quadratic equation ($C_p = AT^{-2} + BT + C$) and a linear equation ($C_p = AT + B$), respectively. In all cases the standard deviation was less than $\pm 1.0\%$. The curve-fitted heat capacity values for all the polymers are given in Table 4. Our data for PXE are in good agreement (maximum deviation 2%) with earlier heat capacity measurements made by Karasz, Bair, and O'Reilly [13] using adiabatic calorimetry.

To further analyze the heat capacity data for the brominated samples, we determined if the measured heat capacities could be related to the mole fraction of brominated units ($\bar{x}$). It was found that in the glassy state heat capacity varies linearly with $\bar{x}$ at all temperatures (310 − 470 K). A typical plot at 400 K is shown in Fig. 7. In each case the data were additive to $\pm 1.8\%$. The heat capacities of molten brominated polymers with $\bar{x} > 0.75$ showed positive (endothermic) deviations from linearity. A typical plot (at 580 K) is given in Fig. 7. For copolymers with $\bar{x} < 0.75$ the heat capacity data are additive within $\pm 0.6\%$. The data for molten PBr$_{\bar{x}}$XE copolymers with $\bar{x}$ equal to 0.87 and 0.94 are higher by 2−5%. These deviations increase with increasing degree of bromination at each temperature. Thermogravimetry suggests that these deviations are the result of thermal degradation.

Corrected heat capacity values for samples undergoing thermal decomposition below 590 K were obtained by extrapolating the data for copolymers with $\bar{x} < 0.75$. These corrected values are given in Table 4 in parentheses. Also listed in Table 4 are

Table 4

Heat capacities of poly(2,6-dimethyl-1,4-phenylene oxide) and its brominated derivatives in $Jmol^{-}K^{-1}$

T, K	$\bar{x}$						
	0	0.25	0.50	0.75	0.87	0.94	1.00
310	148.9	153.4	163.6	163.4	167.7	170.6	173.8
320	153.5	157.4	168.1	166.9	171.3	175.1	177.9
330	157.9	161.3	172.4	170.5	175.0	179.5	182.0
340	162.2	165.2	176.7	174.1	178.8	183.9	186.1
350	166.3	169.1	180.8	177.8	182.5	188.2	190.2
360	170.4	173.0	184.9	181.5	186.4	192.5	194.2
370	174.3	176.9	188.8	185.3	190.2	196.8	198.3
380	178.1	180.8	192.7	189.1	194.1	201.0	202.3
390	181.8	184.7	196.6	193.0	198.1	205.2	206.3
400	185.5	188.5	200.3	196.9	202.0	209.4	210.4
410	189.0	192.4	204.1	200.8	206.0	213.5	214.4
420	192.5	196.2	207.7	204.8	210.0	217.6	218.4
430	196.0	200.1	211.4	208.8	214.0	221.8	222.4
440	199.4	203.9	214.9	212.8	218.1	225.8	226.3
450	202.7	207.8	218.5	216.8	222.1	229.9	230.3
460	206.0	211.6	222.0	220.8	226.2	234.0	234.3
470	209.3	215.4	225.5	224.9	230.3	238.0	238.3
480	[a]	219.3	229.0	229.0	234.4	242.0	242.2
490	243.7	223.1	232.4	233.1	238.5	246.0	246.2
500	246.6	[a]	235.8	237.2	242.6	250.0	250.2
510	249.5	257.9	239.2	241.3	246.7	254.0	254.1
520	252.5	260.2	[a]	245.4	250.9	258.0	258.1
530	255.4	262.6	274.0	249.5	255.0	[a]	262.0
540	258.3	265.0	275.7	[a]	[a]	[a]	[a]
550	261.3	267.3	277.4	284.8	288.0 (288.7)[b,c]	(290.9)[b,c]	[a]
560	264.2	269.7	279.1	286.4	290.6 (289.9)[b,c]	296.0 (292.6)[b,c]	— (293.9)[c]
570	267.1	272.1	280.8	288.0	293.2 (291.1)[b,c]	299.1 (293.1)[b,c]	— (294.9)[c]
580	270.0	274.4	282.4	289.6	295.7 (292.3)[b,c]	302.3 (294.2)[b,c]	— (295.8)[c]
590	273.0	276.8	284.1	291.3	298.3 (293.9)[b,c]	305.4 (295.4)[b,c]	— (296.9)[c]
600	275.9						

[a] Glass transition region
[b] Heat capacity values corrected for thermal degradation (see text)
[c] Heat capacity values obtained from additivity (see text).

similarly extrapolated heat capacity values for PBr_1XE for which direct measurements were not possible due to even greater degradation.
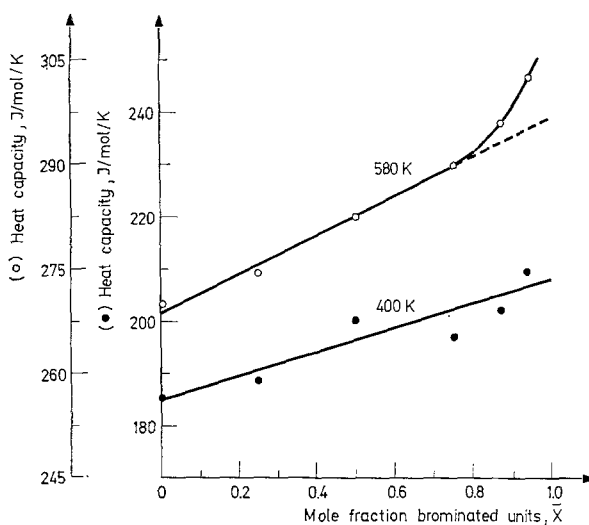
Fig. 7. Effect of the degree of bromination on the heat capacity of $PBr_{\bar{x}}XE$ copolymers in the glassy (400 K) and molten (580 K) states

Discussion

Homopolymers and random copolymers of identical average molecular length have been analyzed. The chemical structure and thermal stability of these materials have already been discussed in the preceding section (see also Figs 2 to 4 and Tables 1 and 2). A more detailed discussion of the glass transition temperature and heat capacities is given next.

Effect of composition on T_g

The glass transition temperature of the copolymers increases nearly linearly with $\bar{x}$ (see Eq. (3) and Fig. 5). Comparison of the data with the Fox equation [10]

$$\frac{1}{T_g} = \frac{(1 - M_2)}{T_{g1}} + \frac{[M_2}{T_{g2}} \tag{4}$$

shows good agreement with an average deviation of ± 2.2 K. T_{g1} and T_{g2} are the glass transition temperatures of PXE and PBr_1XE, i.e., 482 and 559 K, respectively. M_2 is the mass fraction of brominated units. Somewhat better agreement (average deviation ± 1.6 K) is found with the Wood equation [11].

$$T_g = T_{g1} + (kT_{g2} - T_{g1})M_2/[1 - (1 - k)M_2] \tag{5}$$

where k is an empirical constant (0.719).

In the case of homogeneous polymer blends, Couchman [14] has shown that Eqs (4) and (5) can be obtained from the following expression

$$\ln T_g = \frac{M_1 \Delta C_{p1} \ln T_{g1} + M_2 \Delta C_{p2} \ln T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}} \qquad (6)$$

where the subscripts 1 and 2 refer to the corresponding homopolymers. Equation (6) is derived from consideration of the mixed system entropy with the assumption that the excess entropy of mixing for macromolecules is negligible. To obtain the Fox equation from Eq. (6), $\Delta C_p T_g$ for each component is assumed to be equal, while a form of the Wood equation is obtained assuming the ratio of the T_g's of the pure components is not far from unity [14].

It would be useful to determine if Eq. (6) could also predict the compositional dependence of the glass transition temperature for homogenous, statistical copolymers. A comparison of T_g values calculated from Equations (4 – 6) with the experimental results is given in Table 3. We find that Eqs (4) and (5) give significantly better fits to the experimental data than does Eq. (6). Note that in the case of the Fox equation [Eq. (4)] the assumption $\Delta C_{p1} T_{g1} \sim \Delta C_{p2} T_{g2}$ does not hold. The values for PXE and PBr$_1$XE are 13.6 and 10.1 kJ mol^{-1}, respectively. The assumption used to derive a form of the Wood equation from Eq. (6) is perhaps more valid, i.e., $T_g(\text{PBr}_1\text{XE})/T_g(\text{PXE}) = 1.2$, but in this case the parent expression does not fit the experimental results as well as the supposed derived equation.

Considerable improvement in the fit of our data can be obtained by incorporating the measured temperature dependence of ΔC_p for the homopolymers into the Couchman approach. Since the heat capacities of both polymers are closely approximated by linear functions of temperature, ΔC_p for each will also follow a linear dependence (see Eqs (8) and (9), below). For a two component system, the temperature dependence of ΔC_p is substituted into Eq. (5) of Reference 14,

$$X_1 \int_{T_{g1}}^{T_g} \Delta C_{p1} \, \mathrm{d}\ln T + X_2 \int_{T_{g2}}^{T_g} \Delta C_{p2} \, \mathrm{d}\ln T = 0$$

where X is the mole fraction of components 1 and 2. This yields then Eq. (7) instead of Eq. (6),

$$(X_1 A_1 + X_2 A_2)T_g + (X_1 B_1 + X_2 B_2)\ln T_g -$$
$$- X_1 A_1 T_{g1} - X_2 A_2 T_{g2} - X_1 B_1 \ln T_{g1} - X_2 B_2 \ln T_{g2} = 0 \qquad (7)$$

where A and B are the slope and intercept of the linear equation for the temperature dependence of ΔC_p. Predicted values of T_g using Eq. (7) (Table 3) show considerable improvement in the fit with the experimental data relative to the Eq. (6). The simpler Eqs (4) and (5) represent the data still better.

Effect of composition on C_p and ΔC_p

Figure 7 shows that the heat capacity of the homopolymers and copolymers is strictly additive as observed earlier for several other systems (15).

The heat capacity increment (ΔC_p) at T_g was determined for each sample simply as the difference in the heat capacities of the melt and glass taken at the temperature of half "unfreezing" of holes in the polymer glass upon heating [16]. The results are given in Table 3 and Figs 7 and 8. Clearly, the degree of bromination has little effect on ΔC_p up to $\bar{x} \sim 0.75$, with an average value of 28.3 $Jmol^{-1}K^{-1}$ found. At higher degrees of bromination, however, ΔC_p decreases significantly. For example, ΔC_p for PBr_1XE is 18.0 $Jmol^{-1}K^{-1}$ or 36% less than the average value found for polymers with $\bar{x} < 0.75$.
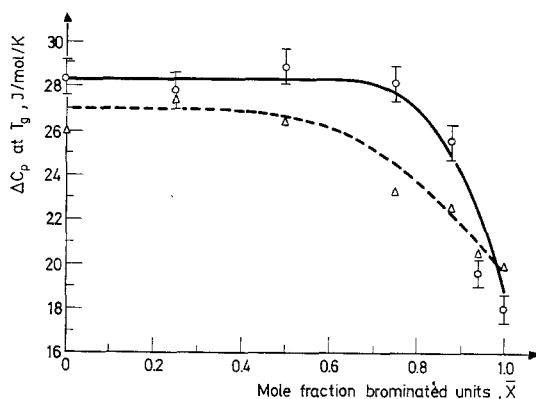

Fig. 8. Effect of the degree of bromination on ΔC_p at the glass transition. Drawn-out curve: experimental data. Dashed curve: calculate dusing Equations (8) and (9) and the experimental glass transition temperatures

In a review of some forty-one monomeric and polymeric glasses, Wunderlich [16] reported that ΔC_p apparently assumes a constant value of 11.3 $\pm$ 2.1 $Jmol^{-1}K^{-1}$ when normalized for the appropriate number of mobile units or "beads" per molecule. For the case of PXE and its brominated derivatives, two beads are present per repeat unit, i.e., the 2,6-dimethylphenylene group and the ether oxygen. Consequently, ΔC_p for copolymers with $\bar{x} < 0.75$ is 14.2 $Jmol^{-1}$ (bead)K^{-1}, somewhat higher than the constant value found by Wunderlich, but consistent with the high values observed for other polymers containing aromatic rings [17]. Lower ΔC_p values for copolymers with $\bar{x} > 0.75$ indicate that some additional modification of the "bead model" is needed in the description of this system.

From the study of molecular models and qualitative estimations of melt viscosity during processing, it is apparent that bromination leads to significant restriction of rotational motion about the ether linkage. Reduction in ΔC_p at $\bar{x} > 0.75$, therefore, may signal the point at which further steric hindrance reduces the ability of

the repeating units to individually contribute to the glass relaxation. In the "bead model" this effect is equivalent to increasing the size of the average bead or reducing the number of beads per chain. From the 36% reduction of ΔC_p found with complete bromination of PXE (i.e., the addition of one bromine per repeat unit), we estimate that the number of beads per repeating unit is reduced from 2 to 1.3 by this chain stiffening effect.

From the hole-theory of liquids [18], ΔC_p at the glass transition can be considered as the added contribution to the heat capacity due to hole formation. This contribution follows an exponential dependence on temperature [19]. Over a limited temperature interval, however, ΔC_p may, to a first approximation, be described by the following two experimentally-based linear equations:

$$\Delta C_p(\text{PXE}) = 65.35 - 0.0815\,T \quad \text{J mol}^{-1}\text{K}^{-1} \tag{8}$$

$$\Delta C_p(\text{PBr}_1\text{XE}) = 186.3 - 0.2967\,T \quad \text{J mol}^{-1}\text{K}^{-1} \tag{9}$$

For a copolymer ΔC_p is determined as the sum of the contributions from the PXE and PBr$_1$XE components calculated at the copolymer T_g. A close fit of the calculated values with the experimental results is found as shown in Figure 8.

Conclusions

The thermal properties of PXE and a well-characterized series of brominated derivatives of identical average molecular length have been studied by thermogravimetry and differential scanning calorimetry .Therma ldecomposition in nitrogen proceeds by a one-step process, enhanced by the presence of bromine and producing a black, carbonaceous char. The extent of char formation increases with the degree of bromination. Thermal decomposition in air follows a two-step process. First, non-oxidative decomposition occurs similar to that found with nitrogen and likewise enhanced by the presence of bromine. Second, oxidative decomposition occurs at about 800 K, resulting in virtually complete volatilization of the remaining material. In contrast to the initial process, oxidative decomposition is unaffected by the extent of bromination.

The effects of decomposition are detected by DSC at temperatures as low as 550 K as endothermic shifts in heat capacity for the more highly brominated polymers ($\bar{x} > 0.75$). Otherwise, heat capacities in the glassy and melt states are found to be additive. Moreover, from the principle of additivity, the heat capacity was estimated at temperatures where accurate measurement was precluded by decomposition.

The heat capacity increment (ΔC_p) at T_g was found to assume a constant value of 28.3 Jmol^{-1}K^{-1} for $\bar{x} < 0.75$. At higher bromine levels, ΔC_p decreases to a value of 18.0 Jmol^{-1}K^{-1} for PBr$_1$XE homopolymer. This behavior is attributed

to the temperature dependence of ΔC_p and is thought to reflect the inability of the repeating units to individually contribute to the glass relaxation due to increased chain stiffness.

The glass transition temperatures of PBr_xXE polymers were found to follow a nearly linear function of the concentration of brominated units. Good fits of the experimental results were obtained using the empirical equations of Fox [10] and Wood [11]. Less satisfactory results were obtained from the Couchman [14] equation derived for blends. However, considerable improvement of the Couchman approach was obtained after taking into account the temperature dependence of ΔC_p.

*

References

1. E. P. CIZEK, U.S. Patent No. 3,383,435 (May 14, 1968).
2. A. S. HAY, P. SHENIAN, A. C. GOWAN, P. F. ERHARDT, W. R. HAAF and S. E. THERBEGE, Encyclopedia of Polymer Science and Technology, *Vol. 10*, Interscience Publishers, A Div. of John Wiley and Sons, Inc., New York, 1969, p. 92.
3. R. P. KAMBOUR, R. C. BOPP, A. MACONNACHIE and W. J. MACKNIGHT, Polymer, 21 (1980) 133.
4. R. P. KAMBOUR, J. T. BENDLER and R. C. BOPP, submitted to Macromolecules.
5. D. M. WHITE and C. M. ORLANDO, paper No. 12 in Polyethers, ACS Symposium Series No. 6, p. 178, Amer. Chem. Soc., Washington, D.C., 1975.
6. D. M. WHITE and H. S. KLOPFER, paper No. 11 in Polyethers, ACS Symposium Series No. 6, Amer. Chem. Soc., Washington, D.C., 1975.
7. D. M. WHITE, unpublished results.
8. P. J. FLORY, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York, 1953, p. 611.
9. C. H. M. JACQUES and H. B. HOPFENBERG, Polym. Eng. Sci., 14 (1974) 441.
10. T. G FOX, Bull. Amer. Phys. Soc., 1 (1956) 123.
11. L. A. WOOD, J. Polymer Sci., 28 (1958) 319.
12. U. GAUR, A. MEHTA and B. WUNDERLICH, J. Thermal Anal., 13 (1978) 71.
13. F. E. KARASZ, H. E. BAIR and J. M. O'REILLY, J. Polymer Sci., Part A-2, 6 (1968) 1141.
14. P. R. COUCHMAN, Macromolecules, 11 (1978) 1156.
15. B. WUNDERLICH and H. BAUR, *Fortschr. Hochpolym. Forsch.*, 7, 151 (1970).
16. B. WUNDERLICH, J. Phys. Chem., 64 (1960) 1052.
17. U. GAUR and B. WUNDERLICH, Polym. Div. Amer. Chem. Soc. Preprints, 20 (1979) 429.
18. N. HIRAI and H. EYRING, J. Polym. Sci., 37 (1959) 51.
19. B. WUNDERLICH, D. M. BODILY and M. H. KAPLAN, J. Appl. Phys., 35 (1964) 95.

ZUSAMMENFASSUNG — Das thermische Verhalten von Poly(2.6-dimethyl-1.4-phenylenoxyd) (PPO^R-Harz), Poly(3-brom-2.6-dimethyl-1.4-phenylenoxyd) und einer Reihe von statistischen Copolymeren dieser Verbindungen mit gleicher durchschnittlicher Moleküllänge wurde durch Thermogravimetrie und Differential-Scanning-Kalorimetrie mit Computerinterface charakterisiert. Die Wärmekapazitäten sind hinsichtlich der Konzentrationen der beiden Komponenten additiv. Die Veränderung in der Wärmekapazität beim Übergang zum Glas (ΔC_p) ist unabhängig von der Zusammensetzung bei Bromierung bis zu 75 % der wiederholungseinheiten. Bei höheren Bromierungsgraden nimmt ΔC_p abrupt ab. Dieses Verhalten wird der Temperaturabhängigkeit von ΔC_p der beiden Komponenten zugeschrieben. Die Glasübergangstemperatur (T_g) der Copolymeren verändert sich nahezu linear mit der Zusammensetzung. Ein Vergleich der experimentellen Werte von T_g wird mit verschiedenen für statistische Copolymere und Mischungen homogener Polymere abgeleiteten Gleichungen ausgeführt. Eine die Temperaturabhängigkeit von ΔC_p berücksichtigende Modifikation der Gleichung von Couchman wird angegeben.

Резюме — С помощью термогравиметрии и дифференциальной сканирующей калориметрии, сопряженной с ЭВМ, охарактеризовано термическое поведение поли (2,6-диметил-1,4-фениленокиси), поли(3-бром-2,6-диметил-1,4-фениленокиси) и ряда их статистических кополимеров с одинаковой средней длиной молекул. Найдено, что теплоёмкости являются аддитивными в отношении концентраций двух компонент. Изменеие теплоёмкости при темперетуре стеклообразования (ΔC_p) не зависило от состава бромированных повторяющихся звеньев вплоть до 75%. При более высоком уровне бромирования C_p резко уменьшается. Это явление обусловлено температурной зависимостью ΔC_p двух компонент. Температура стеклообразования $T_{cт.}$ сополимеров почти линейно изменяется с составом. Проведено сравнение экспериментальных значений $T_{cт.}$ с температурами, установленными на основе различных уравнений для статистических сополимеров и смесей гомогенных полимеров. Представлено видоизмененное уравнение Коухмана, учитывающее температурную зависимость ΔC_p.