670 cm^{-1}, which was reported to be a measure of the conformational change of poly(L-aspartic acid) chain from α-helical to random coil conformation.[10]

Thus, with a membrane from the polyvinyl–polypeptide graft copolymer, the permeability of ions as well as nonelectrolytes may be controlled over a wide range by changing pH as an external stimulation.

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Registry No. (1)·(BMA)·(BLA-NCA) (copolymer), 102493-23-2; (1)·(BMA)·(BLG-NCA) (copolymer), 102493-24-3.

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Synthesis and Properties of Carboxylated Poly(2,6-dimethyl-1,4-phenylene oxide) and Its Ionomer

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ABSTRACT: Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been carboxylated by using butyllithium in a mixed solvent of THF and toluene to form metalated PPO and then treating with carbon dioxide to form carboxylated PPO. A range of polymers containing from 1.5 to 41.7 mol % carboxyl groups was prepared by this reaction scheme. These carboxylic acid polymers were further reacted by esterification or metalization to form esters and sodium or cesium salts. The structure of carboxylated PPO (C-PPO) was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Glass transition temperatures, melting temperatures, decomposition temperatures, and crystallinities of C-PPO are reported. It is found that the T_g of the salt form of C-PPO increases dramatically when the carboxyl group component is more than 5.3 mol %. However, the ester form T_g shows a decrease with increasing substituent concentration. The crystallinities of C-PPO decrease as the degree of carboxylation increases. The cesium salts are the least thermally stable among those studied. Decarboxylation occurs above 350 °C for the acid form of C-PPO.

Introduction

Since the commercialization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), a wide range of applications[1] has developed. Physical aspects of PPO such as thermodynamic properties,[2] morphologies,[3-5] thermal properties,[6] and dielectric properties[7] have been studied extensively. However, relatively few studies have been reported on the chemical modification of PPO. Hay and Chalk[8] discovered a facile method for metalating PPO under a variety of conditions, and this has led to our interest in studying the carboxylation of PPO. In the present investigation, this metalated PPO is used as a typical organometallic material for further polymer modification by a series of reactions to introduce carboxyl groups, carboxylic ester groups, and salt carboxylate groups into the PPO molecular chains. Our purpose was twofold: first, to examine the features that distinguish carboxylated PPO from unmodified PPO and second, to determine if a threshold concentration of ionic groups exists above which clusters form with resulting marked changes in properties.

In this study we have used thermal, dynamic mechanical, and wide-angle X-ray scattering (WAXS) techniques to investigate three forms of carboxylated PPO: acid, ester, and salt. These three functional groups are located in pendant positions on the PPO methyl groups.

The results of thermal and dynamic mechanical studies demonstrate that the nature of these pendant groups plays an important role in determining the glass transition temperatures of these materials. Moreover, the WAXS data demonstrate that the concentration of ionic groups affects the degree of crystallinity. At low levels of carboxylation, the materials behave in general very much like PPO but this behavior is modified significantly as the level of carboxylation is increased. Evidence is presented for the existence of ionic clusters by means of thermal analysis. We have found a critical ion concentration (5.3 mol %) above which clusters may exist. At high carboxylation levels (above 17 mol %) their salt forms display a significantly broadened T_g.

Experimental Section

Materials. The starting PPO was purchased from Aldrich Chemical Co. It was used as received without further purification other than drying at 100 °C for 24 h in a vacuum oven prior to use. The molecular weight was measured by GPC (M_n = 29 244; M_w = 67 559).

Tetrahydrofuran was refluxed over calcium hydride for 2 days and then distilled to remove water, peroxide inhibitor, and other impurities. Toluene was refluxed over phosphorus pentoxide and was distilled.

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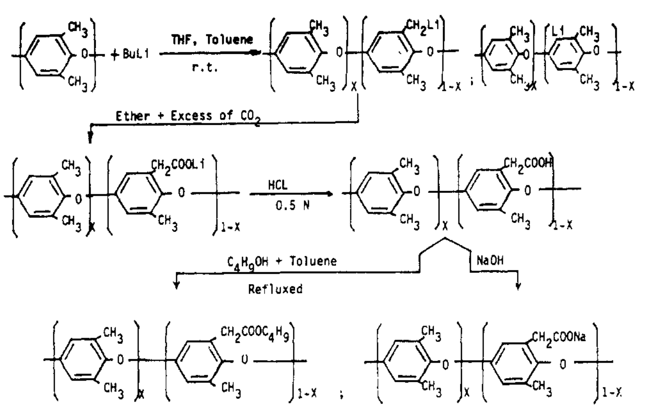
Scheme I



Butyllithium in hexane (1.6 M) was purchased from Aldrich Chemical Co. Since most alkyllithium solutions deteriorate after the container is opened, the concentration of butyllithium must be frequently checked during the metalation reaction. A convenient method[9] was used here.

Reactions. The PPO was metalated by using a series of ratios of initial butyllithium to PPO in a mixed-solvent system of THF and toluene (4:1 by volume) at room temperature under a dry nitrogen flow. The metalated material was carboxylated by pouring the reaction mixture into an excess of solid carbon dioxide in ether and by precipitating the suspension into a large excess of hexane. This reactant was further acidified by using dilute hydrochloric acid and was then washed with distilled water and dried in vacuo at 110 °C for 2 days.

The carboxylated PPO was esterified by using an excess of butyl alcohol which was refluxed in toluene with a small amount of HCl until the reactant mixture appeared as a clear solution and until the amount of extracted water was constant. The mixture was precipitated in an excess of hexane which had been dried in vacuo at 110 °C for 2 days.

To prepare sodium or cesium carboxylate, the resultant carboxylic acid was neutralized with either sodium hydroxide or cesium acetate, depending on the desired salt. The reactant was washed with water to remove excess NaOH or CH_3COOCs and was then dried in vacuo at 220 °C for 3 days. The reaction scheme is summarized in Scheme I.

Characterization. The structures of carboxylated PPO (C-PPO) were confirmed by IR and NMR spectroscopy, elemental analysis, and titration.

Infrared spectra of KBr pellets of the polymer were obtained with a Perkin-Elmer 1320 infrared spectrophotometer. The determination of the carboxylation level by IR analysis was based on the ratio of the absorption at 1700 cm^{-1} (carboxyl group stretching vibration) to the absorption at 1600 cm^{-1} (aromatic ring stretching).

NMR measurements were carried out on chloroform solutions of PPO or C-PPO. ^1H NMR and ^{13}C NMR were used to determine the location of the carboxyl group on the polymer chain. All of the NMR measurements were performed with high-resolution Varian XL-300 and Varian XL-200 NMR instruments.

Elemental analysis was performed by the Analytical Services and Microanalytical Laboratory, University of Massachusetts. The estimation of the degree of carboxylation was based on the following calculation:

$$\text{COOH mol \%} = \frac{O_{\text{C-PPO}}\ \% - O_{\text{PPO}}\ \%}{O_{\text{1-subt-PPO}}\ \% - O_{\text{PPO}}\ \%} \tag{1}$$

Here $O_{\text{C-PPO}}$ % is the oxygen percentage in C-PPO, O_{PPO} % is the oxygen percentage in PPO, equal to 13.33%, and $O_{\text{1-subt-PPO}}$ % is the oxygen percentage in a substituted PPO with one carboxyl group per repeat unit, equal to 23.17%.

The degree of carboxylation was determined by titration by using 0.1 N methanolic potassium in dioxane. Ethanol containing 1% thymol blue was used as an indicator.

Measurements. DSC measurements were carried out with a Perkin-Elmer DSC II. The scanning speed was 20 °C/min in all cases and indium was used as a standard. The temperature range scanned was from 400 to 550 K; the peak temerature of the melting endotherm was taken as the melting point of the polymer. The glass transition temperature was taken to be the midpoint of the change in heat capacity.

Table I
Relationship between Reaction Condition and Degree of Carboxylation

sample	[Li]/[PPO], mol:mol	COOH, mol % elem anal.	COOH, mol % titration in dioxane	solvents
C-1	1.5:1	57.0	41.7	H_2O + NaOH
C-2	1.0:1		23.1	swelling in H_2O + NaOH
C-9	1.0:2	40	24.7	swelling in H_2O + NaOH
C-10	1.0:3	20	15.8	swelling in dioxane
C-14	1.0:3	14	10.0	$CHCl_3$, dioxane
C-13	1.0:4	4.9	5.3	$CHCl_3$, dioxane, toluene
C-11	1.0:5	1.5	1.5	$CHCl_3$, dioxane, toluene

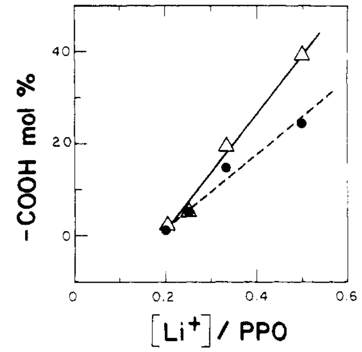


Figure 1. Effect of [Li^+] concentration on COOH mole percent in the reaction system. The COOH mole percent was measured by titration (●) and elemental analysis (△).

Dynamic mechanical measurements were carried out with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) operated in the three-point bending mode.

The temperature range was from 100 to 280 °C at a rate of 5 °C/min. The samples, which were compression molded at 250 °C under vacuum, were measured under a nitrogen environment at a frequency of 1 Hz.

The thermal stability of the polymers was determined with a Perkin-Elmer TGS-2 analyzer. The temperature range was from 50 to 900 °C at a scanning rate of 10 °C/min in a nitrogen atmosphere.

WAXS measurements of C-PPO were carried out with a Philips-Norelco wide-angle goniometer which was equipped with a graphite monochromator. The goniometer was used in the symmetrical reflection mode in order to obtain good resolution of the crystalline diffraction peaks.

Results and Discussion

Characterization of the Carboxylation of PPO. A series of carboxylated PPO (C-PPO) samples were obtained by varying the ratios of butyllithium to PPO. The reaction conditions employed and the characterization data for the samples investigated are collected in Table I. It is seen that the degree of carboxylation is determined primarily by the amount of butyllithium added to the polymer solution. For low [Li]/[PPO] ratios, a linear relationship between Li concentration and degree of carboxylation was obtained as shown in Figure 1.

The polymers prepared range in degree of carboxylation from 1.5 to 41.7 mol %. The solubility of C-PPO varies with the carboxyl group content. Acid forms of C-PPO are soluble in several organic solvents as shown in Table I, depending on the degree of carboxylation. At the highest carboxyl group content, C-PPO is only soluble in alkaline

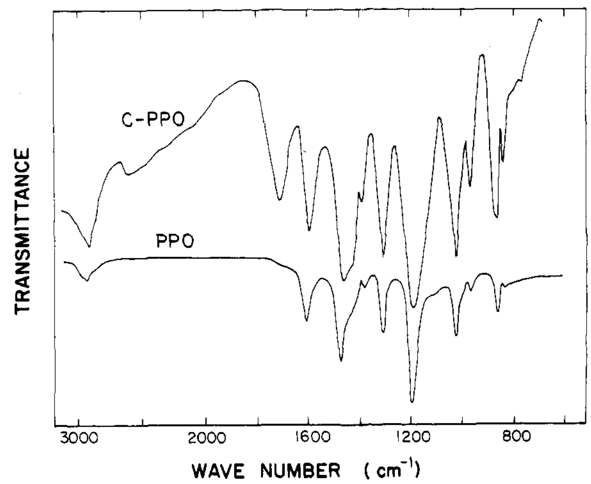


Figure 2. IR spectra of PPO and C-PPO.

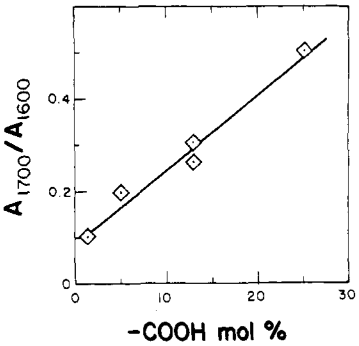


Figure 3. Correlation between the absorption ratio A_{1700}/A_{1600} and COOH mole percent. COOH was measured by titration analysis.

water, which suggests polyelectrolyte behavior. This indicates that carboxylation levels as high as 41.7 mol % can be achieved without cross-linking by this reaction.

Salt forms of C-PPO are insoluble even in polar organic solvents. However, the ester forms of C-PPO dissolve in various organic solvents, similar to unmodified PPO.

As shown in Figure 1, the degree of carboxylation obtained from the elemental analysis method deviates from that of the titration method. In the following, data obtained by the titration method will be used.

Infrared Spectra Analysis. In addition to the chemical method (titration analysis results), evidence that carboxyl groups have been successfully added to the PPO chains is found in the infrared spectra of these modified materials. Figure 2 shows the infrared spectrum of the starting PPO and one of its carboxylated derivatives. The carboxylated polymer shows a new absorption peak at 1700 cm^{-1} which is assigned to the carboxylic acid carboxyl stretching vibration (O=C—O).

When the ratio of the integrated absorbances of the carboxyl group stretching vibration at 1700 cm^{-1} and the aromatic ring vibration at 1600 cm^{-1} is plotted as a function of carboxylate content (as determined by titration), the linear correlation shown in Figure 3 is obtained. This demonstrates that infrared spectroscopy can serve as an analytical technique for estimating the degree of carboxylation.

Additional evidence for the existence of carboxyl groups in the modified material is provided by ^1H NMR and ^{13}C NMR spectra of C-PPO, as shown in Figures 4–6. In comparison to the starting material, PPO, the ^1H NMR spectrum of carboxylic acid PPO (Figure 4) shows a new peak at 3.47 ppm, while the ^{13}C NMR (Figure 5) shows a new peak at 34.7 ppm. These peaks can be assigned to the

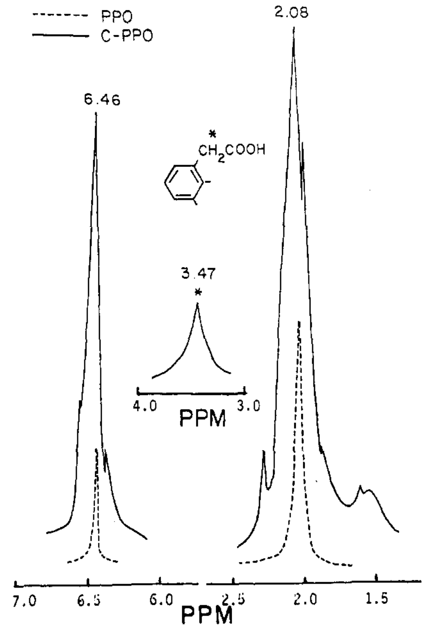


Figure 4. ^1H NMR spectra of PPO and C^{10}-PPO. C^{10} means 10 mol % carboxylation.

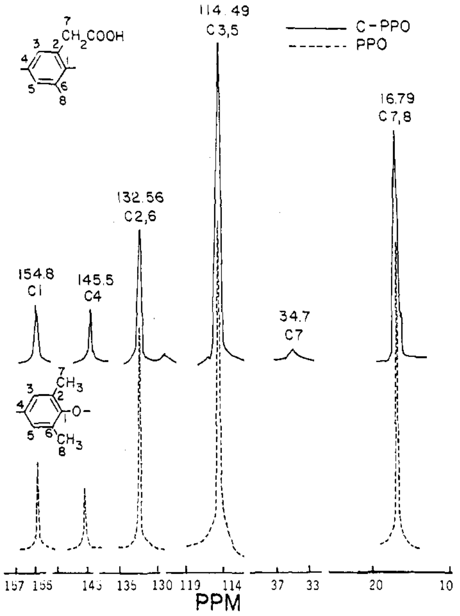


Figure 5. ^{13}C NMR spectra of PPO and C^{10}-PPO. C^{10} means 10 mol % carboxylation.

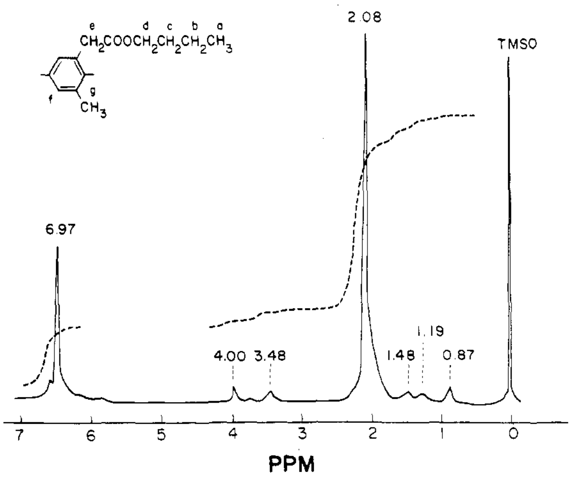


Figure 6. ^1H NMR spectrum of carboxylic ester PPO. The ester group is $COOC_4H_9$.

Table II
Crystallinities of Carboxylated PPO

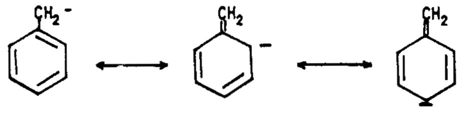
			$W_x = \sum I_i/[\sum(I_i + I_a)]$ (by WAXS)	
sample	COOH, mol %	$W_x = (\Delta H_i/\Delta H_f)$, % (by DSC)	powder sample	amorphous film[a]
PPO	0	38.0	30.5	35.6
C-11	1.5	38.0	41.5	
C-13	5.3	41.0	42.2	38.1
C-14	10.0	31.0	31.2	25.5
C-10	15.8	23.0	26.3	21.0

		W_x	
sample	sodium salt, mol %	by DSC	by WAXS
C-11-Na	1.5	33.0	
C-13-Na	5.3	24.0	34.3
C-14-Na	10.0	13.0	26.3

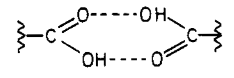
[a] Recrystallized in a solvent vapor.

methylene proton and the methylene carbon, respectively, on the aromatic ring.

Figure 6 shows the ^{1}H NMR spectrum of the butyl ester derivative. The methyl and methylene proton signals of the butyl ester ($COOCH_2CH_2CH_2CH_3$) are well resolved at 0.87, 1.19, 1.48, and 3.97 ppm, respectively, and the methylene proton on the aromatic ring is still at 3.47 ppm. These results indicate that the carboxyl group preferentially adds to the methyl group. This is consistent with the greater stability of a benzyl anion over that of an aryl anion. The former is believed to be more stable due to resonance.[8]



In the present study, neither the proton nor the carbon atom of the carboxyl group can be detected directly. This may be caused by the formation of hydrogen-bonded carboxyl groups. In carboxylic acid containing polymers, hydrogen-bond formation between carboxylic acid groups is essentially complete at room temperature.[11-14] The hydrogen-bonded carboxylic acid is a dimer



with a resultant absorbance at 1700 cm^{-1} in the IR spectrum. This is consistent with our IR result. For our samples, nearly all of the carboxyl group absorbances appear at 1700 cm^{-1}.

Properties of Carboxylated PPO. Crystallinities. The low carboxylation level C-PPO obtained by precipitating from solvents is a partially crystalline material. The crystallinities were estimated by WAXS and DSC data. For WAXS measurement, the fractional crystallinity W_x of the polymer was calculated from the relation

$$W_x = K\sum I_c/[\sum(I_c + I_a)] \qquad (2)$$

where $\sum I_c$ and I_a represent the integrated intensities of the resolved crystalline reflections and of the amorphous scattering. K is a constant, accounting for the relative scattering efficiency per unit mass of the amorphous and crystalline phases, here taken as unity.

In DSC measurements, the fractional crystallinity W_x' of C-PPO was estimated by the quantity

$$W_x' = \Delta Q_f/\Delta H_f \qquad (3)$$

where ΔQ_f is an observed fusion enthalpy proportional to the area under the DSC endotherm and ΔH_f is the heat of fusion of the completely crystalline PPO, taken as 42 ± 8 J/g.[2]

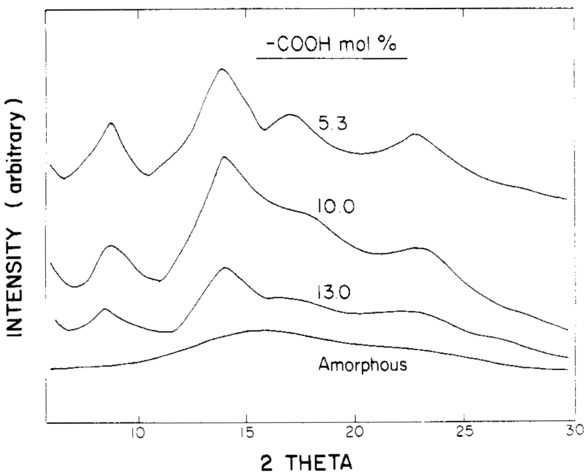


Figure 7. Wide-angle X-ray scattering (WAXS) curves of C-PPO's.

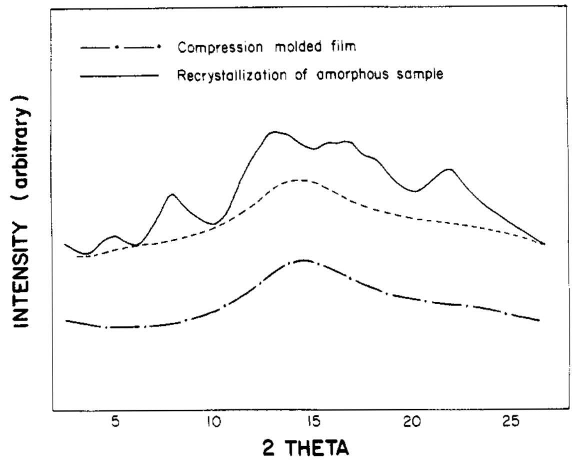


Figure 8. WAXS curves of C-PPO.

The crystallinity of C-PPO is summarized in Table II. The scattering patterns are shown in Figure 7. These results indicate that the degree of crystallinity in C-PPO decreases with increasing carboxyl group content; no crystallinity is observed in samples with carboxylation levels above 25 mol %.

We previously reported that bulk PPO could be crystallized by exposure to solvent vapor to the extent of about 30%.[3] In this study, the amorphous carboxylated PPO film obtained by compression molding was exposed to an atmosphere of *n*-butanone vapor. The sample was recrystallized as shown in Figure 8. Its degree of crystallinity was approximately equal to that of the powder sample.

Thermal Properties of Carboxylated PPO. The DSC results for the carboxylic acid, butyl ester, and sodium carboxylate PPO samples are displayed in Figures 9 and 10. In this study, a series of carboxylated PPO derivatives with a range of 4.5–22.7 mol % carboxyl group was studied. The results for the acid-form C-PPO powder samples are shown in Figure 9. The solitary feature in the curves is a melting peak which broadens with increasing carboxyl group content. The maxima of these peaks lie around 521 ± 2 K. The areas under the peaks correspond to the experimental heat of fusion ΔQ_f, which decreases with the degree of carboxylation. This is consistent with the WAXS data mentioned above. The T_g's of samples obtained by quenching and then reheating are shown in Figure 9b. The T_g increases slightly with increasing carboxylation due to hydrogen-bonding between the carboxylic acid groups.[13,14]

Table III
Characterization Data for Carboxylated PPO's

			acid		ester		salt
sample	mol % carboxylation	% neutralization[a]	T_g, K	$\Delta C_p \times 10^2$	T_g, K	$\Delta C_p \times 10^2$	T_g, K
C-11	1.5		487				488
C-37	4.5	90	489	5.90	474	4.27	492
C-34	6.7		490	5.14			
C-38	7.7				457	4.96	515
C-14	9.9		491				536
C-36	11.5	83	492	5.46	465	5.45	541
C-39	17.5	94	494	5.14	455	5.83	591
C-26	22.7	84	501	6.05	451	5.19	603

[a] Measured by elemental analysis.

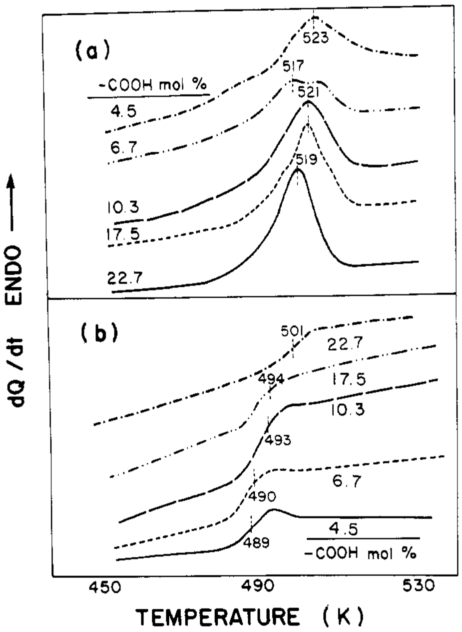


Figure 9. DSC curves for acid-form C-PPO's: (a) as received; (b) on reheating.

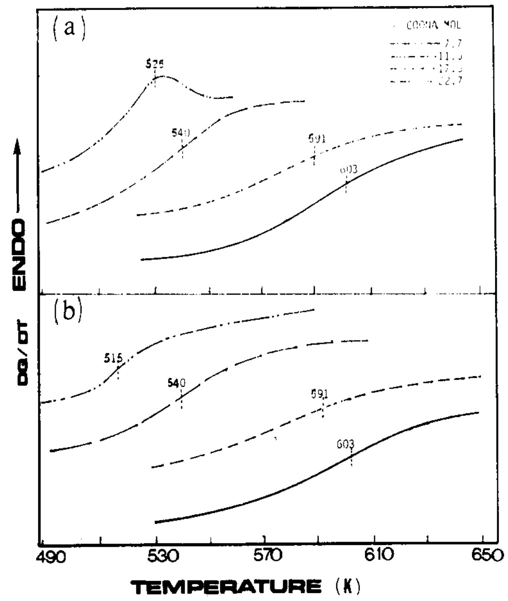


Figure 10. DSC curves for sodium salt form C-PPO: (a) as received; (b) on reheating.

In the salt form of C-PPO (Figure 10), a broad imperfect melting peak is observed, but only for the low degrees of ionization. In highly carboxylated samples, where the concentration of ions is above 11.5 mol %, the endothermic peak disappears and the glass transition extends over a substantial temperature range. For the ester-form C-PPO samples, the effects of substituents are the opposite of those described above. Apparently the large ester groups increase chain flexibility or free volume so T_g decreases noticeably as the number of pendant groups increases. A comparison of acid, ester, and salt forms of C-PPO is given in Figure 11. The T_g's determined by DSC are summarized in Table III. When these T_g's are plotted against the mole percent of carboxylation (as determined by titration analysis) the plot in Figure 12 is obtained. This plot demonstrates a linear relationship with slightly pos-

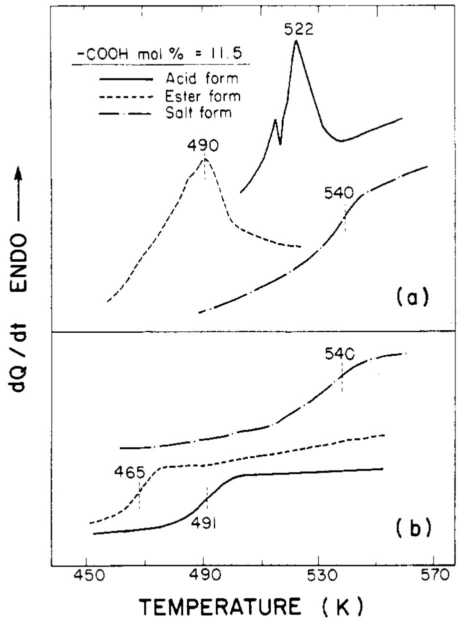


Figure 11. Comparison of acid, ester, and salt forms of C-PPO DSC traces: (a) as received; (b) on reheating.

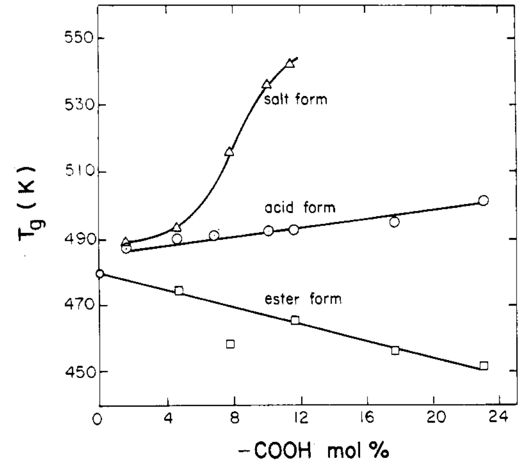


Figure 12. T_g dependencies of COOH mole percent.

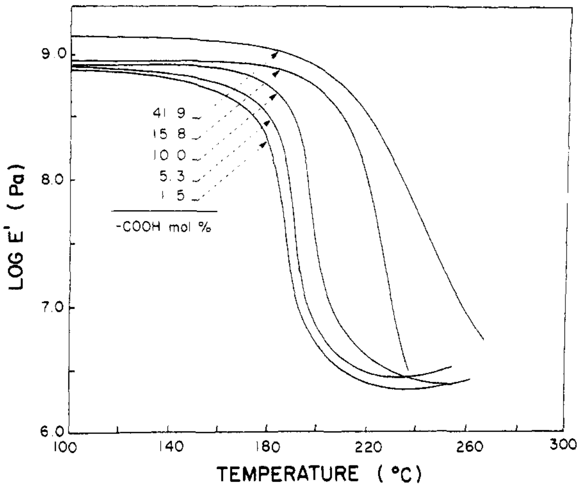


Figure 13. Temperature dependencies of E' at 1 Hz for carboxylic acid PPO's.

itive slope for the acid C-PPO. The sodium salt exhibits a sharply rising slope when the carboxylate content is above 6 mol %. This behavior has been observed in other ion-containing copolymers.[15,16] It has been suggested that a critical concentration of salt groups is necessary for the formation of microphase-separated domains, and this roughly corresponds to the change in slope in the dependence of T_g on salt content. If this is so, Figure 12, top curve, indicates the presence of ionic clusters in PPO's carboxylated above a level of roughly 6 mol %. It is interesting to note that this is the same level of ionic substitution suggested by Eisenberg et al.[17,18] for clustering in styrene–sodium methacrylate ionomers.

Dynamic Mechanical Properties of C-PPO. Figures 13 and 14 show the temperature dependencies of the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) at 1 Hz for the acid form of C-PPO. The E' behavior of C-PPO shown in Figure 13 indicates that the modulus increases with increasing degree of carboxylation. The E'' and tan δ of C-PPO display an obviously broadened relaxation for high levels of carboxylation (Figure 14) and the maximum moves to higher temperatures. There is no evidence for microphase separation. Two separate peaks are observed in tan δ vs. temperature curves for 5.3 and 10 mol % cesium salts of C-PPO as shown in Figure 15. They are labeled β and α in increasing order of temperature. The β peak is assigned to motions accompanying the T_g of PPO and the α peak is assigned to motions accompanying the T_g of the ionic phase. The position of these peaks moves to slightly higher temperatures with increasing substituent content. This is in good agreement with DSC results, where a critical concentration of salt groups is necessary before the T_g begins to deviate from the typical copolymer-type behavior by rising sharply. This may be taken as evidence of ionic clustering in PPO's carboxylated above a level of roughly 5 mol % for the cesium salt and 6 mol % for the sodium salt.

Thermal Stability of C-PPO. The TGA scans for the acid C-PPO are shown in Figure 16. It is seen that the temperature of weight loss onset ranges between 150 and 400 °C and decreases with increasing degree of carboxylation (Figure 16a). Major decomposition occurs above 400 °C. While some of this initial weight loss is probably due to the loss of water, it is apparent that the addition of carboxylic groups to the PPO chain greatly reduces its thermal stability.

A comparison of the acid, ester, and salt forms of C-PPO is shown in Figure 16b. The following order of thermal stabilities is observable: PPO-COOEt > PPO-COOH > PPO-COONa > PPO-CCOCs.

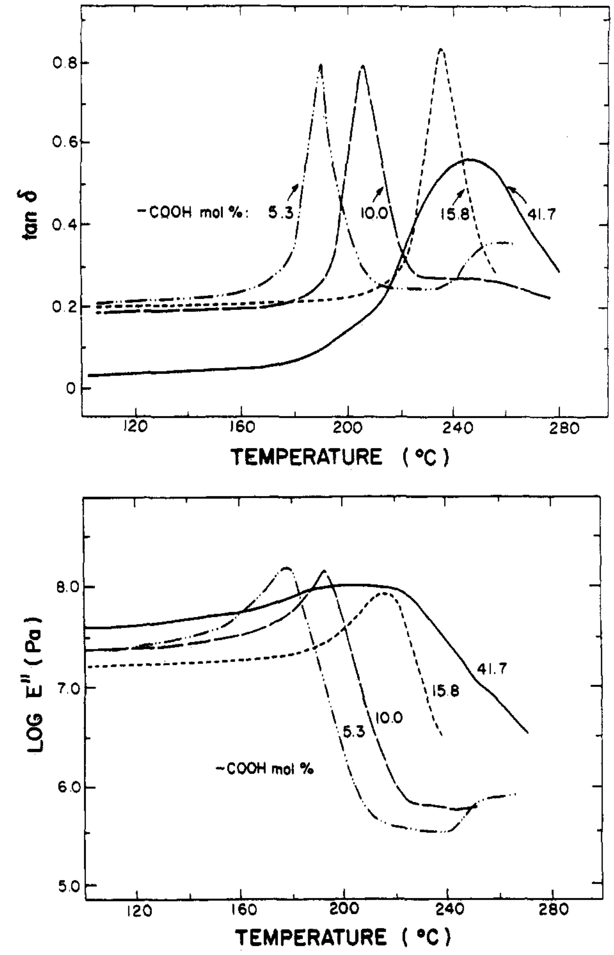


Figure 14. Temperature dependencies of E'' and tan δ at 1 Hz for carboxylic acid PPO's.

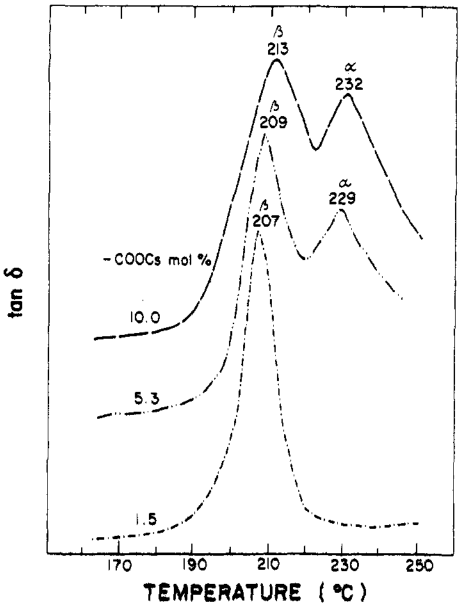


Figure 15. Temperature dependencies of tan δ at 1 Hz for the cesium salt of C-PPO.

In general, polymers with carboxyl groups are rather easy to decarboxylate at high temperatures. The TGA scans show two stages of decomposition in the derivative curve for a sample with a high level of carboxylation. A small amount of decomposition before the major decom-

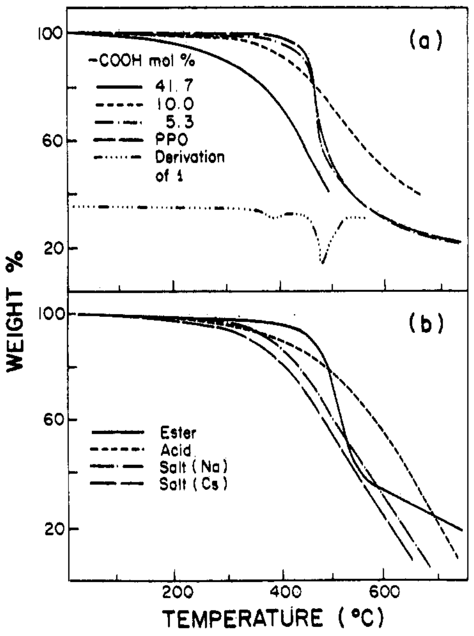


Figure 16. Temperature dependencies of weight loss measured by TGA: (a) acid-form C-PPO's; (b) comparison of acid, ester, and salt forms of C-PPO.

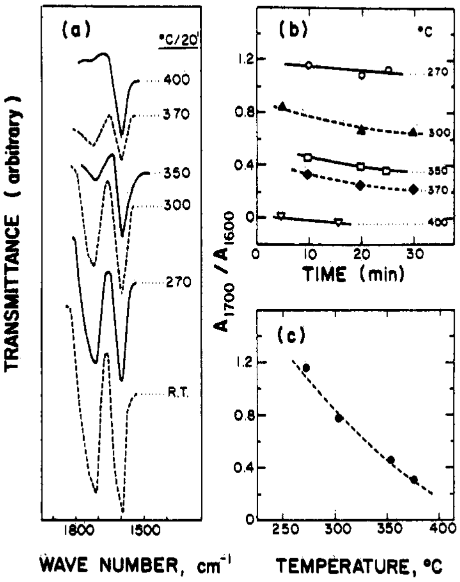


Figure 17. (a) IR spectra for 22.7 mol % carboxylation PPO ($C^{22.7}$-PPO) at different annealing temperatures for 20 min. (b) Annealing time dependencies of the ratio of A_{1700}/A_{1600}. (c) Temperature dependence of the ratio of A_{1700}/A_{1600} for $C^{22.7}$-PPO annealed for 20 min.

position may be attributed to decarboxylation. The evidence for decarboxylation was obtained by IR measurement and is shown in Figure 17. For the IR spectra of a 22.7 mol % carboxyl group content, shown in Figure 17a, the ratio of carbonyl absorbance at 1700 cm^{-1} to aromatic ring absorbance at 1600 cm^{-1} was used to estimate the variation in extent of decarboxylation. The results shown in parts b and c of Figure 17 indicate that decarboxylation does not occur below 270 °C. Above 300 °C, the carboxyl group content in the sample starts decreasing a little. At temperatures higher than this, the typical carboxyl group absorbance decreases rapidly, disappearing completely at 400 °C.

Conclusion

C-PPO's with different carboxyl group contents were obtained by varying the ratio of butyllithium to PPO. NMR spectra indicate that the major position of carboxyl group substitution is on the methyl group. The C-PPO's with low carboxyl group contents, less than 10 mol %, are partially crystalline polymers because the concentration of carboxylate groups is not sufficient to disrupt the formation of crystals. However, highly carboxylated samples display an amorphous morphology because the substituent concentration is sufficient to suppress crystallization. The amorphous samples may be recrystallized by exposing them to appropriate solvent vapors.

For acid C-PPO, the T_g's increase slightly with increasing degree of carboxylation, while ester T_g's decrease with increasing carboxylation. For the salt forms, the DMTA results and DSC results suggest a critical level of carboxylation (5 mol % for DMTA and 6 mol % for DSC) above which clustering becomes detectable.

The carboxylated PPO can be initially decarboxylated between 300 and 400 °C but the majority of decomposition occurs above 450 °C. Thermal stabilities of C-PPO decrease with degree of carboxylation and the ester derivatives have greater stability than the acid or the salt form.

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