Chemical Modification of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) via Phase Transfer Catalysis

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Synopsis

The chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been performed under phase transfer catalyzed (PTC) conditions. Four types of reactions: Williamson etherification, cyanide displacement, esterification, and heterocyclic group transfer have been identified as positive reactions involving the nucleophilic displacement on PPO. In reaction with alcohols, under PTC conditions, functional yields as high as 100% were obtained while for the esterification reaction functional yields of 92% were reached. Low conversions were found in reactions with cyanides and heterocylic compounds. Possible interactions of the reactive sites leading to additional crosslinking are being suggested. Minor changes in thermal stability of substituted PPO compared with the parent polymer were recorded. The modification of their permeation properties to gases was attributed to changes in polymer chain mobility and packing as well as to changes in polymer side chain polarity.

INTRODUCTION

In a previous paper from our laboratory,[1] the chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by electrophilic substitution under Friedel-Crafts conditions has been reported. It was found that a maximum monosubstitution degree of 79.4 could be reached, more than that being difficult to achieve because of both a decrease in the remaining position nucleophilicity and steric hindrances. To further analyze the possibility of introducing a variety of functional groups into this polymer, we have extended our studies to a very versatile method of polymer modification: phase transfer catalysis (PTC).[2-4] This route was particularly attractive because PPO was considered ready to be modified by nucleophilic substitution at the benzylic position while the aromatic backbone could remain inert under PTC conditions.

The application of phase transfer catalysis technique in polymer chemistry has been rapidly growing in recent years and has been explored in development of a new synthetic method of polymer synthesis and structural modification of polymers.[5,6] For example, phase transfer catalysis was applied in the reaction of polychloromethylstyrene[7,8] with carboxylates in the presence of 18-crown-6, and was used to control site–site interactions in the reaction of the same polymer with 1,4-butanedithiol in basic medium.[9] Other examples include the generation of polymer supported ylides,[10] addition reactions,[11] and nucleophilic displacements in polymers.[11-13]

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Among many reactions which can be carried out via phase transfer catalysis, this work is directed to the modification of PPO by Williamson etherification, cyanide and heterocyclic group displacement, and esterification reactions.

EXPERIMENTAL

Materials

PPO[14] and PPO brominated at the benzylic position[15] were synthesized according to the literature procedure: $\overline{M}_n = 17{,}000$, $\overline{M}_w = 51{,}000$, $\overline{M}_w/\overline{M}_n = 3.0$ (determined by gel permeation chromatography, with polystyrene standard). The phase transfer catalysts as well as all the reagents and solvents (Aldrich) were used without further purification.

Synthetic Procedures

The benzylic position of the aromatic structure of PPO was activated towards nucleophilic displacements by bromination of the $-CH_3$ groups.[15]

The nucleophilic substitution reactions on brominated PPO were carried out under liquid–liquid phase transfer reaction conditions, consisting of an organic solvent (benzene) and a concentrated aqueous solution (50%) of the base (NaOH) in the presence of tetrabutylammonium hydrogen sulfate (TBAS) or tetraphenylphosphonium bromide (TPPB). A solid–liquid phase transfer process was employed in cyanide and carboxylate displacements when the nucleophilic reagent was transferred by a crown-ether (18-crown-6). After the required reaction time, the reaction mixture was washed several times with water. The separated polymer solution was dried over $MgSO_4$, filtered, and precipitated into methanol. A final purification was carried out by precipitation of the product from chloroform solution with methanol. The resulting polymer was vacuum dried to constant weight.

Techniques

200 MHz ^{1}H-NMR spectra were recorded from $CDCl_3$ solution and with TMS as internal standard on a Nicolet NT 200 spectrometer. Solid state ^{13}C-NMR spectra were obtained with a Nicolet S 100 spectrometer. FT-IR spectra were recorded from KBr pellets on a Nicolet 60SX spectrophotometer. The thermal behavior of polymers was analyzed on a DuPont differential scanning calorimeter (Model 1090) under nitrogen atmosphere with indium used as a calibration standard. The heating and cooling rates were 10°C/min.

A modified Gilbert cell[16] was used to determine the gas permeation properties of polymer films. The testing area of the film was 45.8 cm^2. The film thickness was in a range of 1.27×10^{-2}–2.81×10^{-2} mm. The test side was exposed to a carbon dioxide : methane : nitrogen mixture in a mole ratio 3.11 : 33.6 : 63.29. The permeant was picked up by a carrier gas, helium, and injected intermittently through a sample valve into a gas chromatograph for analysis. The partial pressure of the test gas was 29.7 psi (0.21 MPa) while the partial pressure of the product gas on the permeant side was held at an insignificant level by purging with 29.77 psi (0.21 MPa) helium at a flow rate much in excess of the permeation rate.

ORGANIC PHASE $\quad$ PPO-CH$_2$Br + (R)$_4$N^{+-}OR$_1$ $\rightarrow$ PPO-CH$_2$-OR$_1$ + (R)$_4$N$^+$Br$^-$

PHASE BOUNDARY $\quad$ ∿∿∿∿∿⏐ ∿∿∿∿∿∿∿⏐ ∿∿

AQUEOUS PHASE $\quad$ NaBr $\quad$ + $\quad$ (R)$_4$N^{+-}OR$_1$ $\rightleftharpoons$ R$_1$O$^-$Na$^+$ $\quad$ + $\quad$ (R)$_4$N$^+$Br$^-$
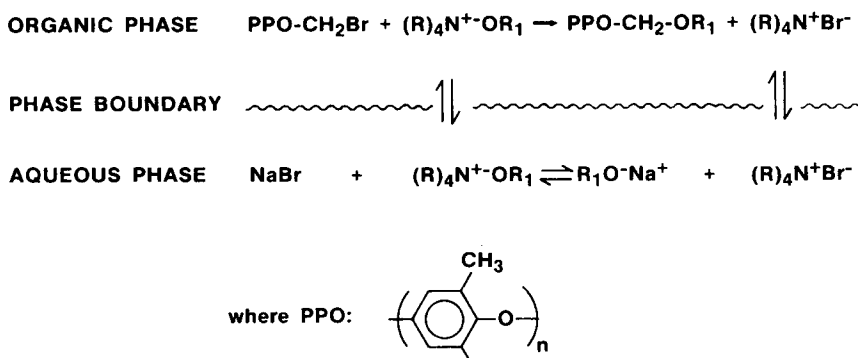
where PPO:

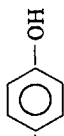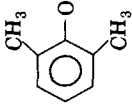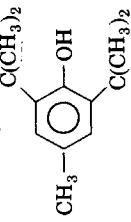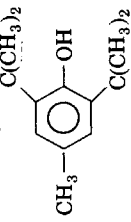Fig. 1. Phase transfer scheme for Williamson etherification of PPO.

RESULTS AND DISCUSSION

Williamson Etherification Reactions on PPO

The phase transfer catalyzed Williamson etherification is significantly easier than that of the traditional one which requires prior generation of the alkoxide salt, normally by reaction of the alcohol with a strong base such as sodium hydride, sodamide, or sodium metal.[17] In the two-phase Williamson ether reaction, the base used is concentrated aqueous sodium hydroxide. The alcohol or the alkyl phenol is deprotonated by hydroxide either in the aqueous phase or at the interface and then solubilized in the organic phase by ion pairing with the quaternary ammonium ion. A generally accepted phase transfer scheme,[17] particularized for Williamson etherification of PPO, is shown in Figure 1. It can be noticed that, after the deprotonation of the alcohol and its ion pairing with the quaternary ion, the reaction occurs between it and the electrophilic polymer chain in the organic phase. The catalytic cycle is completed with the exchange of the nucleofuge for a molecule of nucleophile followed by phase transfer.

The substitution degree determined by ^{1}H-NMR spectroscopy was between 0.2% and 45%, depending on the reaction conditions, the bromination degree of the parent polymer, and the nucleophilicity of the alcohol (Table I). Optimum PTC conditions for the formation of the ether linkage consist of a fivefold excess of 50% aqueous sodium hydroxide and 3–5 mol % of TBAS with vigorous stirring in a temperature range of 60–80°C. Aliphatic primary alcohols gave yields of 50–100%, but the reaction with phenols required longer times and did not give yields higher than 66%. The substituted aromatic alcohols such as 2,6-di-*tert*-butyl-4-methylphenol react very sluggishly, if at all. In this case, PPO with very low degree of bromination was used. It was supposed that, for such bulky nucleophile molecules, the introduction of one substituent group on the polymer chain would retard the introduction of the next group because of the steric effects. The same reaction also has been carried on PPO, which has a higher degree of bromination. Longer reaction times and lower temperatures have been used, but side reactions lead to a crosslinked polymer. The crosslinking reaction considered to be responsible for the crosslinking of the PPO–CH$_2$Br is presented schematically in Figure 2.

TABLE I
Williamson Etherification Reaction on PPO

No.	Catalyst	Modifying agent	Degree of functionality (mol %)	Reaction conditions			Substitution degree[b] (mol %)	Functional yield (%)
				PPO : MA[a] : CAT[a] (mol : mol : mol)	Time (h)	Temp (°C)		
1	TBAS	$CH_3(CH_2)_5OH$	45.0	1 : 5 : 0.25	16	0	45.0	100.0
2	TBAS	$CH_3(CH_2)_6OH$	45.0	1 : 5 : 0.25	8	60	39.8	88.4
3	TBAS	$CH_3(CH_2)_7OH$	45.0	1 : 5 : 0.25	16	80	43.0	95.5
4	TBAS	$CH_3(CH_2)_9OH$	45.0	1 : 5 : 0.25	16	60	37.0	82.2
5	TBAS	$CH_3(CH_2)_{13}OH$	35.0	1 : 5 : 0.25	8	80	23.0	65.7
6	TBAS	$CH_3(CH_2)_{15}OH$	8.2	1 : 4 : 0.20	9	80	2.3	28.0
7	TBAS		45.0	1 : 4 : 0.20	16	80	22.5	50.0
8	TBAS		62.0	1 : 5 : 0.25	10	80	41.0	66.1
9	TBAS		45.0	1 : 5 : 0.25	16	60	Crosslinked	—
10	TBAS		3.6	1 : 3 : 0.15	8	80	0.2	5.56

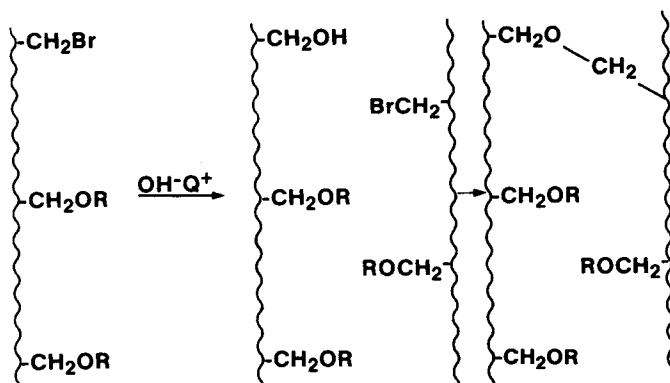[a] MA = modifying agent; CAT = catalyst.
[b] From ^{1}H-NMR spectroscopy.

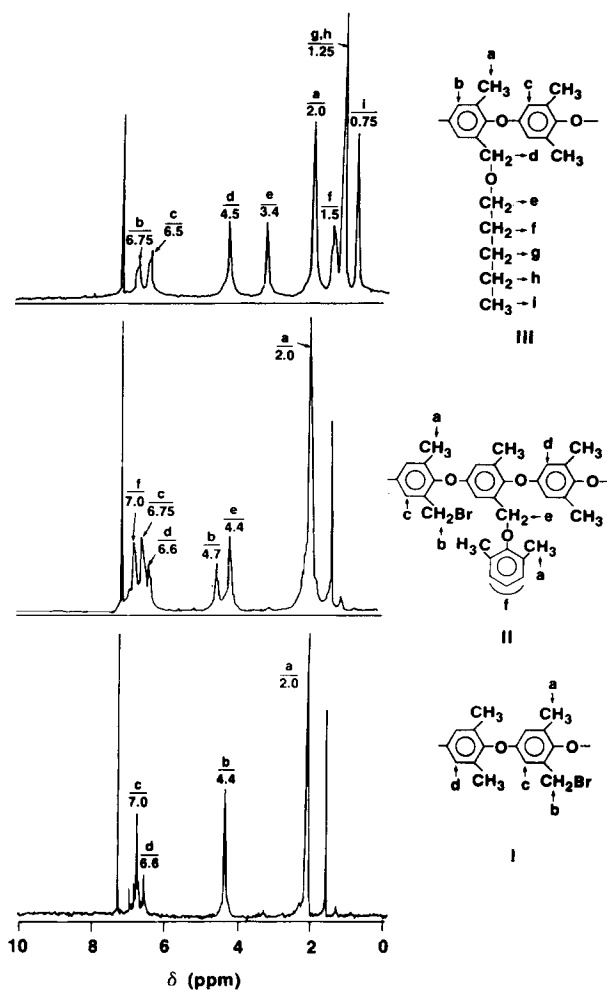Fig. 2.   Possible crosslinking reactions occurring under phase transfer catalyzed conditions.

Fig. 3. ^{1}H-NMR spectra of PPO (I), PPO modified with 2,6-dimethylphenol (II) and PPO modified with 1-pentanol (III).

Consequently, the modified polymers might contain forms of unreacted groups or other functionalities resulting from side reactions. Typical ^{1}H-NMR spectra of the soluble polymers resulted from Williamson etherification of PPO via phase transfer catalysis are presented in Figure 3 together with the assignment of their protonic resonances. The percent of substitution was determined from the ratio of the integrals of proton resonances.

Cyanide Displacement Reactions

No cyanide displacement occurred when a liquid–liquid phase transfer catalyzed reaction was performed in the presence of quaternary ammonium or phosphonium salts (examples 1–3, Table II). By contrast, 18-crown-6 has been found effective in the solid–liquid phase transfer cyanide displacement reaction on PPO. This is due to the fact that crown ethers possess the ability to form complexes with inorganic salts and also to solubilize these salts in aprotic solvents. Comparing KCN and NaCN, the former gives the highest degree of substitution. This is not a surprising result since it is well known[2,3] that the stability of a complex between a crown ether and an alkali metal cation greatly depends on both the size of the inner cavity relative to that of the ion. Of all the alkali metal ions, 18-crown-6 forms the most stable complex with K^+. Even in this case, long reaction times had to be employed in solid–liquid phase transfer cyanide displacements.

Esterification Reactions

Under normal displacement conditions in protic solvents, carboxylate anions are among the weakest nucleophiles. The major factor contributing to their poor performance must be the strong solvation of the anion.
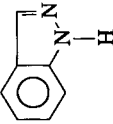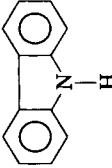
The phase transfer method facilitates the dissolution of carboxylates in nonpolar media. In these solutions, due to the relatively poor solvation of anions, carboxylate is an effective nucleophile and reacts readily with bromomethylated groups of PPO. Both of the catalysts employed, TBAS and 18-crown-6, have been found efficacious for this type of reaction (examples 5 and 6, Table II).

Hetrocyclic Group Displacement

The nucleophilic substitution of methyl brominated PPO with two heterocyclic nucleophiles, carbazole and indazole, has been examined. Using the same parent polymer, the same catalyst and similar conditions of reaction, it appears that the substitution degree for carbazole is higher than for indazole (examples 7 and 8, Table II). The side reactions were also more pronounced in the case of indazole, leading to a crosslinked polymer which was difficult to characterize. From Figure 4, the ^{1}H-NMR spectrum of methyl-brominated PPO modified with carbazole, it is clear that a heterocyclic transfer reaction took place. From integration of signals from 7.0 to 6.0 ppm for the aromatic backbone and from 8.2 to 7.8 ppm for the carbazole substituent (two protons) a substitution degree of 34% has been obtained.

Since an insoluble polymer resulted from the reaction of methyl-brominated PPO with indazole, a solid state ^{13}C-NMR was run. For comparison, a solid state ^{13}C-NMR of the polymer resulting from the reaction of methyl-

TABLE II
Various Reactions on PPO under Phase Transfer Catalyzed Conditions

No.	Catalyst	Modifying agent	Degree of functionality (mol %)	PPO : MA[a] : CAT[a] (mol : mol : mol)	Time (h)	Temp (°C)	Substitution degree[b] (mol %)	Functional yield (%)
					Reaction conditions			
1	TBAS	NaCN	45.0	1 : 5 : 0.25	10	80	0.0	0.0
2	TBAS	KCN	45.0	1 : 5 : 0.25	8	80	0.0	0.0
3	TPPB	KCN	35.0	1 : 3 : 0.15	8	80	0.0	0.0
4	18-Crown-6	KCN	35.0	1 : 5 : 0.25	40	80	5.0	14.2
5	TBAS	CH_3COOK	13.0	1 : 3 : 0.15	5	60	11.0	84.6
6	18-Crown-6	CH_3COOK	13.0	1 : 3 : 0.15	5	60	12.0	92.3
7	TBAS	(structure)	35.0	1 : 5 : 0.25	16	80	Crosslinked	—
8	TBAS	(structure)	35.0	1 : 5 : 0.25	16	80	34.0	96.9

[a] MA = modifying agent; CAT = catalyst.
[b] From ^{1}H-NMR spectroscopy.
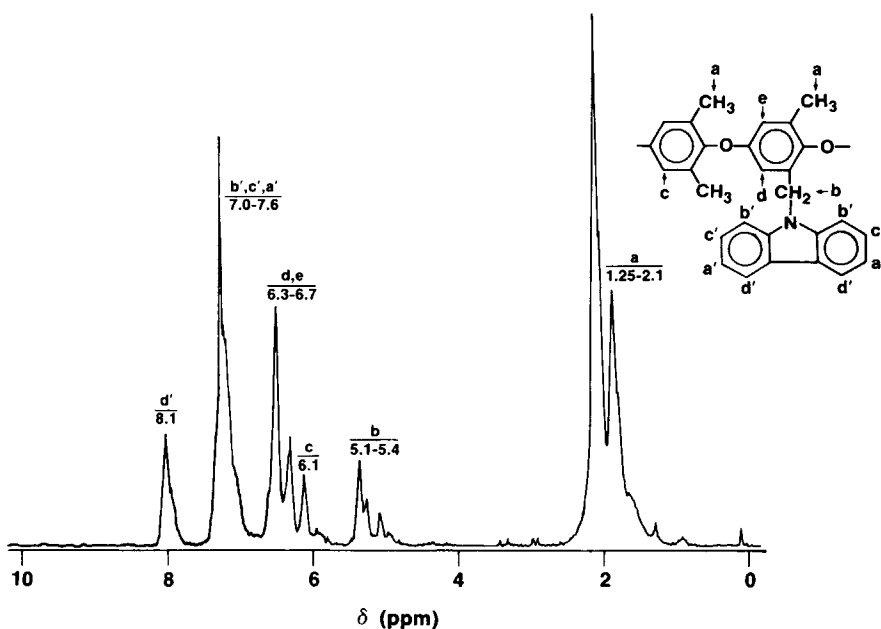
Fig. 4. ¹H-NMR spectrum of PPO modified with carbazole.

brominated PPO with carbazole has been recorded. The spectra are presented in Figures 5 and 6. The solid state ^{13}C-NMR spectrum of the PPO modified with indazole shows a peak at about 30 ppm, which may be due to the occurrence of the substitution reaction to a small extent. The band near 60 ppm can be attributed to the $—CH_2—O—CH_2$ bridges formed by crosslinking reactions as was suggested in Figure 2. There does appear to be a small amount of increase in the aromatic region, indicating also that a small amount of substitution has occurred. The infrared spectrum of this compound (Fig. 7) also indicated in the aromatic region (700–800 cm^{-1}) that a small amount of indazole group has been introduced on PPO.
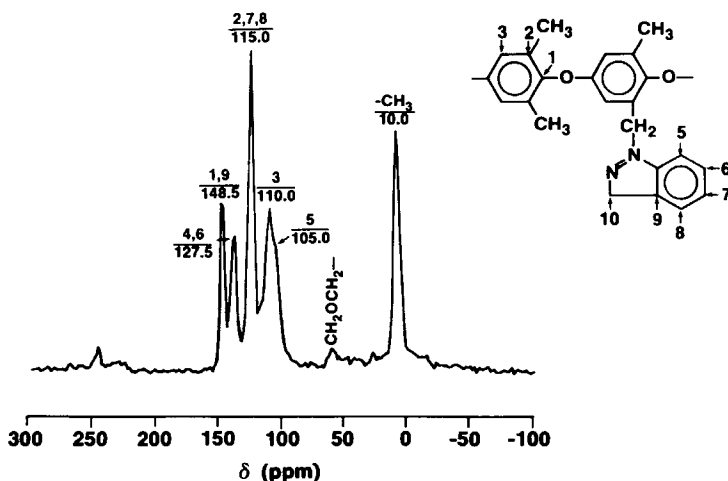

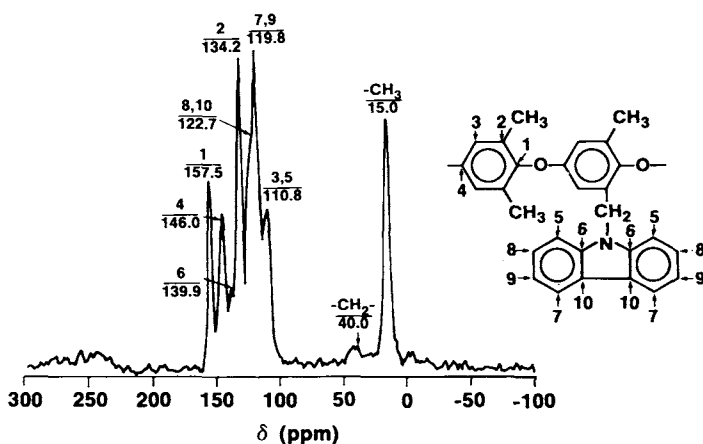Fig. 5. ^{13}C-NMR spectrum of PPO modified with indazole.

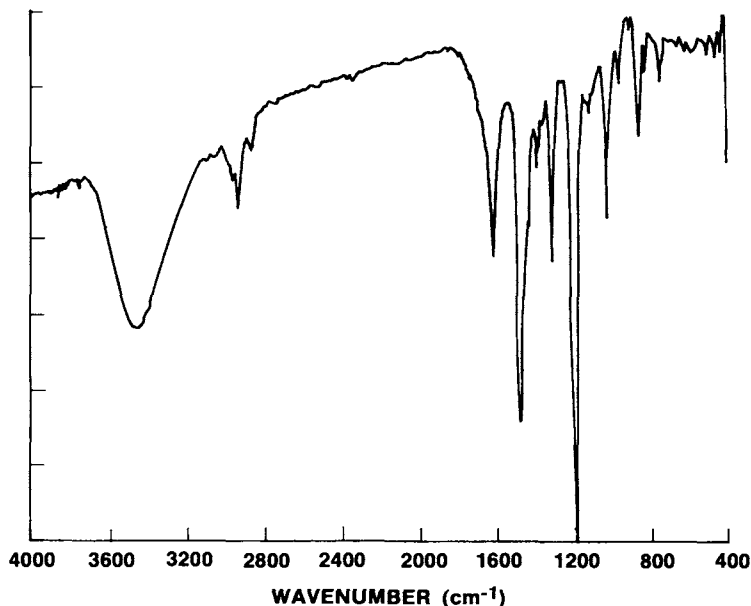Fig. 6. ^{13}C-NMR spectrum of PPO modified with carbazole.

Fig. 7. FT-IR spectrum of PPO modified with indazole.

THERMAL CHARACTERIZATION OF THE MODIFIED PPO

Both thermogravimetric analysis and differential scanning calorimetric studies have been performed on modified and unmodified PPO samples. Table III presents the weight losses and the glass transition temperatures (T_g) of the most representative polymers.

The change of T_g with introducing aromatic rigid side groups is a result of two effects:

(a) the introduction of aromatic side chains reduces backbone mobility and free volume;

(b) the increased number of side chains increases the intermolecular packing distances.

TABLE III
Thermal Characterization of PPO Modified by PTC

No.	Modifying agent	Number Corresponding, Tables I or II	Zone I		Zone II		T_g (°C)
			Temp range (°C)	Weight loss (%)	Temp range (°C)	Weight loss (%)	
1	None	—	175–300	0.3	300–400	0.6	212
2	Bromine (3.6 mol %)	—	225–375	5.7	375–400	6.4	210
3	1-Octanol	3, Table I	185–300	0.2	300–400	3.9	75
4	Decyl alcohol	4, Table I	145–250	0.7	150–300	3.2	70
5	Potassium cyanide	4, Table II	100–175	0.0	175–400	10.0	218
5	Potassium acetate	6, Table II	50–175	1.0	175–400	10.6	135
7	Nonylphenol	7, Table I	175–245	2.5	245–400	16.6	280
8	2,6-Dimethylphenol	8, Table I	100–200	0.0	200–275	6.7	167

TABLE IV
X-Ray Diffraction of Some Polymers Obtained from PPO
under Phase Transfer Catalyzed Conditions

No.	Modifying agent	Number corresponding, Tables I or II	Crystallinity degree (%)	Peak 1 2θ (Å)	Peak 2 2θ (Å)
1	None	—	23	4.10	4.80
2	1-octanol	3, Table I	19	4.50	5.80
3	Decyl alcohol	4, Table I	31	4.50	5.80
4	Hexadecanol	6, Table I	15	4.14	6.01
5	p-Nonylphenol	7, Table I	20	4.01	5.37
6	2,6-Dimethylphenol	8, Table I	23	4.05	4.58
7	Potassium cyanide	4, Table II	14	3.34	5.53
8	Carbazole	8, Table II	13	4.26	5.88

Because a decrease in T_g value for PPO substituted with aromatic side groups was observed, it can be supposed that the second effect has more influence than the first one. Introducing flexible side groups also results in an increase of intermolecular distances; consequently, free volume predominates and the T_g value is lowered. This can be exemplified with PPO modified with long side chains such as: $-O-(CH_2)_n-CH_3$, where $n = 7$–9. In all these cases the T_g was substantially lowered, being a function of the substitution degree of the parent polymer and of the length of the side chain. No lateral crystallization was observed by DSC for these widely spaced comblike polymers. They showed rather broad endotherms on DSC thermograms, indicating a very low degree of crystallinity. This was confirmed by X-ray analysis as is shown in Table IV, which presents the crystallinity degree and peaks modification of some of the substituted structures.

GAS PERMEATION PROPERTIES OF THE MODIFIED PPO

As with any other macroscopic physical properties, the gas transport properties of polymers can be ascribed to a certain extent to the conformational characteristics of their molecular structure. The main chain flexibility of the polymer and the segmental mobility of the polymer chains play an important role in gas transport phenomena in polymers. Modifications of molecular structure that alter polymer chain molecular motions cause changes in gas transport properties, as well. The polymer permeability for various gases can be described as

$$P = S \times D$$

the product of the solubility coefficient and diffusion coefficient of the gas molecules in the polymer.[18] The permeation properties of PPO, PPO substituted with polar groups, aromatic rigid groups and hydrocarbonic long chains, to a carbon dioxide, methane, nitrogen mixture are presented in Table V. Separation factors determined from the same ternary gas mixtures are also given in Table V. The separation factor or selectivity (α) for a gas a over a gas

No.	Modifying agent	P_{CH_4} (barrer)[b]	P_{CO_2} (barrer)[b]	$\alpha^c_{CO_2/CH_4}$
1	None	3.30	64.0	19.20
2	Potassium cyanide	1.38	30.1	21.80
3	Carbazole	1.01	18.2	18.02
4	1-Nonanol	3.11	24.10	7.75

[a] Testing temperature = 25°C.
[b] 1 barrer = $10^{-10}[cm^3(STP)cm]/[cm^2$ sec cm Hg].
[c] α = separation factor.

b in a mixture is given by

$$\alpha^a_b = Pa/Pb$$

where P_a and P_b are the mean permeability coefficients for gases a and b.

From Table V it can be seen that a decrease in permeability for both gases CO_2 and CH_4 is obtained for PPO modified with KCN. This decrease is slightly higher for CH_4 than for CO_2 leading to a separation factor

$$\alpha_{CO_2/CH_4} = 21.80$$

which is superior to that of PPO. Since the permeability for both gases decreases almost in the same ratio, it is difficult to decide whether solubility (S) or diffusion (D), or both, are responsible for this effect. However, by introduction of polar side groups such as —CN, an increase of the cohesive forces between chains can be expected. The segmental mobility decreases and therefore the permeation and diffusion rates also may decrease. Restrictions of chain mobility brought about by aromatic rigid side groups as in the case of PPO substituted with carbazole result in a decrease in permeability for both gases CO_2 and CH_4, with no increase in selectivity. Other modifications such as introduction of long side chains (example 4, Table V) may enhance the local chain segmental mobility. An increase in permeability must generally result from the increase in frequency and/or amplitude of the cooperative molecular motions in the polymer. However, the nature of the side chains is equally important. As can be seen from Table V, for the tested gas mixture, the permselective properties of PPO modified with long side groups such as —O—$(CH_2)_8CH_3$, are rather poor. The permeability for CH_4 remains almost unchanged whereas the permeability for CO_2 significantly decreases. Therefore, such a modification of the polymer structure cannot serve for the enhancement of the separation factor in polar gas/hydrocarbon separations but may prove useful for hydrocarbon/hydrocarbon separations.

CONCLUSIONS

Chemical modification of PPO has been realized under phase transfer catalyzed conditions by nucleophilic substitution of the benzylic position of PPO. Four types of reactions—Williamson etherification, cyanide displace-

ment, heterocyclic group transfer, and esterification reactions—have been identified as positive reactions on PPO using PTC technique. The nucleophilic substitution occurs easily with alcohols when a functional yield as high as 100% was obtained. The esterification reaction reaches a reasonable yield; meanwhile, the cyanide displacement and heterocyclic transfer reaction are very slow reactions. During some of these reactions, side reactions are favorized, and the final polymer results in a crosslinked form. The thermal stability of the modified polymers does not change very much when compared with that of the parent polymer. The changes in glass transition temperatures of these polymers follow the expected trends. The modification of their permeation properties to gases was attributed to both changes in polymer chain mobility and packing as well as to changes in the side chain polarity.

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