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Benzoylation of polyphenylene oxide: Characterization and gas permeability investigations

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Abstract

Benzoylation of polyphenylene oxide (PPO) was carried out with aromatic acid chlorides bearing specific groups at *para*-position (H, methyl, Br, Cl and nitro), which differ in their polarity and bulk. The reaction conditions were optimized individually to get the high degree of substitution. These materials were characterized for thermal as well as other physical properties that are known to affect the gas permeation. In a series investigated, the nitrobenzoyl substitution on PPO resulted in the highest increase in glass transition temperature and the lowest thermal stability. An estimation of the packing density parameters—fractional free volume by density measurement and the *d*-spacing by X-ray diffraction analysis showed an increase in the packing density. The gas permeability was found to decrease in all the cases of benzoylation. The helium and oxygen based selectivities were increased, while CO_2 based selectivities were decreased. The unusual trend observed in the gas permeation properties is explained on the basis of nature of substituent and the degree of substitution.

Keywords: Polyphenylene oxide; Benzoylation; Gas permeability; Selectivity

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1. Introduction

Among various glassy polymers, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has high gas permeability and moderate selectivity. Its high permeability stems from larger diffusion coefficients of gases in PPO as compared to other polymers [1]. In addition, PPO is a versatile material for performing chemical modification on its backbone. The different types of groups can be substituted either on the phenyl ring or on the methyl group of PPO with an appreciable degree of substitution and ease. Effects of various substituent groups on the gas permeation properties are reported in the literature. These include sulfonation [2,3], bromination [4,5], silylation [6], Friedel–Crafts reactions [7], nitration [8], carboxylation [3,5] etc. The substitution by an inorganic sulfonate group on PPO rendered more rigidity to the chain and greatly decreased the free volume that determines the low gas permeability and the high selectivity [2,3]. Chawdhury et al. [3] showed that the introduction of a polar group such as –COOH or $–SO_3H$ to the aromatic ring of the PPO backbone increased permeability

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ratio, the effect being stronger for $–SO_3H$ substitution rather than for –COOH substitution. It was also shown that the loss in permeability due to a polar group substitution ($–SO_3H$) could be compensated by using bromination and sulfonation combinely. The PPO-aryl bromination was found to be an effective way of changing the packing state and the torsional motion of the aromatic constituent in the main chain [4]. This study also revealed that the solubility of CO_2, CH_4 and N_2 in the PPO increased with an increasing extent of the bromination and the change was larger for a gas with lower condensability. In the case of bulky trimethylsilyl substitution [6], the gas diffusivity increased; while, when it was replaced by a triphenylsilyl group, the diffusivity decreased. In the case of Friedel–Crafts sulfonylation [7], a small decrease in CH_4 permeability and an increase in CO_2 permeability is reported; while acylation by long chain acid resulted in a large increase in CH_4 permeability while maintaining CO_2 permeability. The aryl-nitration of PPO and PSF backbone decreased the gas permeability, but the selectivity was increased [8]. It was also expected that the nitro substituent on the aryl backbone restricted segmental torsional mobility. Other PPO modifications like acylation [9], amination via nitration [10], incorporation of the amide groups by electrophilic substitution with isocyanates [11], are also reported. Thus, high intrinsic permeability, moderately high T_g and ease of chemical modification of various types made this polymer an attractive material for investigations towards improvement of its gas permeation properties by chemical modification of its backbone.

Above literature reports indicated that the nonpolar substitution like silylation increased the gas permeability, while the polar group substitution like carboxylation, sulfonation, nitration etc. improved selectivities in compensation with a general decrease in gas permeability. It is also known that the substituent on the phenylene of the polymer main chain affects the gas permeability in modified PPO more significantly than the substituent on the methyl side group [6]. Smaller group substitution by the sulfonylation and a long chain containing acylation had opposite effects on CH_4 and CO_2 permeability behavior [7]. In the present work, it was thought to investigate effects of the phenyl ring substitution of the PPO backbone by a group that is simultaneously bulky as well as polar in nature. Thus, benzoylation of the PPO phenylene ring using reactive *para*-substituted aromatic acid chlorides was performed. This type of substitution is expected to induce bulk (by the substituted benzoyl group) and polarity (by carbonyl of the benzoyl group) simultaneously. The *para*-substituted aromatic acid chlorides were selected for the benzoylation since they are expected to be moderately rigid and bulky. The effects of substitution on the physical as well as the gas permeation properties of these modified PPO are investigated.

2. Experimental

2.1. Materials and monomers

The benzoyl chloride, *p*-chlorobenzoic acid, *p*-nitrobenzoic acid, *p*-toluic acid, thionyl chloride, 1,2-dichloroethane, toluene, cupric chloride and anhydrous aluminum chloride (all LR grade) were procured from S.D. fine chemicals (India). The *p*-bromobenzoic acid was procured from Merck (India) Ltd. The 2,6-dimethyl phenol and morpholine were procured from Aldrich Chemicals, USA. All the aromatic acids were used as-received for their conversion to respective acid chloride. All the pure gases (He, Ar, N_2, O_2, CO_2 and CH_4) used for permeability measurements had the minimum purity of 99.5%.

2.2. PPO synthesis

The PPO was synthesized from 2,6-dimethyl phenol dissolved in tolune:ethanol mixture (4:1) in the presence of morpholine and cupric chloride as per the reported procedure [12]; except a small variation of prolonged period of oxygen blanketing (14 h). The spectral analysis by IR and ^1H NMR as well as glass transition temperature of this material were in agreement with the literature data [7]. The intrinsic viscosity determined by graphical method using toluene as a solvent was 2.3 dl/g.

2.3. Preparation of acid chloride

The aromatic acids used in this work; viz. *p*-chlorobenzoic acid, *p*-nitrobenzoic acid, *p*-toluic acid and *p*-bromobenzoic acid were converted to the respective acid chloride using thionyl chloride. The *p*-toluoyl chloride, *p*-bromobenzoyl chloride and *p*-chlorobenzoyl chloride were purified by the fractional distillation under reduced pressure; while, *p*-nitrobenzoyl chloride was purified by the recrystallization from the dry petroleum ether. These acid chlorides were stored under dry atmosphere until use.

2.4. Benzoylation of PPO

The Friedel–Craft benzoylation reactions were carried out using $AlCl_3$ as a Lewis acid catalyst and 1,2-dichloroethane as the solvent. The reaction conditions were set for individual cases and are as given in Table 1. In a typical procedure, 2 g of PPO was dissolved in 60 ml of 1,2-dichloroethane with stirring for 6 h under nitrogen blanketing and at the ambient temperature. To this solution, already prepared complex of an anhydrous aluminum chloride (1 molar equivalent, 2.22 g, 0.166 mol) and an acid chloride (1.1 molar equivalent, 0.183 mol) in 10 ml of 1,2-dichloroethane was added dropwise for a period of 5–10 min at the ambient tem-