Gas Sorption and Transport in Poly(phenylene Oxide) and Comparisons with Other Glassy Polymers

K. TOI,* G. MOREL,† and D. R. PAUL, *Department of Chemical Engineering, University of Texas, Austin, Texas 78712*

Synopsis

The sorption and transport of several gases in poly(phenylene oxide) were measured at 35°C, and the results have been analyzed in terms of the dual sorption/mobility models which have been successfully employed for this purpose for other glassy polymers. Both the extent of sorption and rate of permeation of gases are quite large for poly(phenylene oxide) compared to other glassy polymers with rigid chain backbones. It is shown that the high extent of sorption is owing to the high glass transition temperature of this polymer, but this is not a significant factor in its high permeability to gases. The latter stems from large diffusion coefficients. It is shown that the capacity of the Langmuir mode of sorption inherent to glassy polymers is related to the value of the glass transition temperature in a general way for a wide variety of polymers. Observations about the diffusion coefficients for numerous gas–polymer pairs are discussed.

INTRODUCTION

Detailed knowledge and understanding about the sorption and transport of gases in glassy polymers is critical for the logical use of these materials in certain packaging applications and in membrane separation processes. It is now well established for glassy polymers that both sorption and transport involve nonlinear responses to gas pressure in contrast to the linear relationships, viz., Henry's and Fick's laws, which well describe the behavior for gases in rubbery polymers. Mathematical models envisioning dual mechanisms of sorption and transport have been developed which accurately describe the nonlinearities characteristic of the glassy state, and an important goal presently is to relate the terms of these models to polymer structure in a quanitative manner. A base of data is developing which should eventually lead to such relationships. The present paper is concerned with gas sorption and transport in poly(phenylene oxide) (PPO), which has been selected because it is an important engineering thermoplastic and because it has rather unique gas permeation characteristics. The latter point is made in Table I where permeability coefficients for N_2 and CO_2 in a variety of amorphous polymers having widely varying glass transition temperatures are compared.[1] Of these polymers, PPO has the highest T_g; yet, with the exception of natural rubber, PPO is the most permeable to gases. It is somewhat surprising that a rigid polymer like PPO is over an order of magnitude more permeable than a soft material like butyl rubber. Of course, the latter polymer is well known for its gas barrier characteristics, but, nevertheless, Table

---

* Permanent address: Department of Chemistry, Tokyo Metropolitan University, Setagaya, Tokyo, Japan.

† Permanent address: Laboratoire de Recherche sur les Macromolecules, Universite Paris-Nord, 93430 Villetaneuse, France.

Journal of Applied Polymer Science, Vol. 27, 2997–3005 (1982)
CCC 0021-8995/82/082997-09$01.90

TABLE I
Permeabilities of Several Amorphous Polymers at 25°C

Polymer	T_g (°C)	$P \times 10^{10}$ (cm^3 (STP)·cm/cm^2·s·cm Hg)	
		N_2	CO_2
Butyl rubber	−76	0.324	5.18
Natural rubber	−72	9.43	153.0
Poly(ethyl methacrylate)	65	0.220	5.0
Poly(vinyl chloride)	82	0.0118	0.157
Polystyrene	100	0.788	10.5
Polycarbonate	150	0.30	8.0
Poly(phenylene oxide)	220	3.81	75.7

I makes the point that polymer segmental mobility factors, on the scale which determine the location of the glass transition, have little to do with gas permeation.

This paper presents detailed data for the behavior of several gases in PPO analyzed in terms of the nonlinear models mentioned earlier and compares these results with other polymers for which comparable studies have been made.

EXPERIMENTAL

The PPO used was supplied to us by A. S. Hay and J. C. Golba of the General Electric Co. It has $\overline{M}_n = 22{,}600$, $\overline{M}_w = 34{,}000$, and $\overline{M}_z = 57{,}200$, as determined by light scattering gel permeation chromatography. Solutions containing 10% PPO in trichloroethylene were cast into thin film using a spin-casting device similar in design to that described by Koberstein and Cooper.[2] This approach permitted a vacuum-temperature protocol that produced a film free of residual solvent and PPO crystallinity as detected by DSC.

Sorption and permeation measurements were made at 35°C using facilities and procedures described previously.[3–5]

RESULTS

Figure 1 shows sorption isotherms for four gases in PPO. Each curve exhibits a similar nonlinear pattern observed for other glassy polymers[6–8]; however, the extent of sorption is significantly larger than that seen with other polymers in previous studies. The data for each gas is well described by the following dual sorption model,

$$C = k_D p + \frac{C'_H bp}{1 + bp} \tag{1}$$

and the parameters shown in Table II, deduced by a nonlinear regression routine, give the optimum fit of the model to the data. The limiting slopes at high and low pressures, k_D and $k_D + C'_H b$, respectively, in terms of eq. (1), for each isotherm may be correlated with the Lennard–Jones potential well depth, ϵ/k, as shown in Figure 2 and as previously demonstrated for other polymers.[6–8]

The permeability of these gases was found to vary with upstream driving pressure p_2, in accord with the following model used in the earlier studies mentioned above:

$$P = k_D D_D + \frac{C'_H b\, D_H}{1 + bp_2} \tag{2}$$

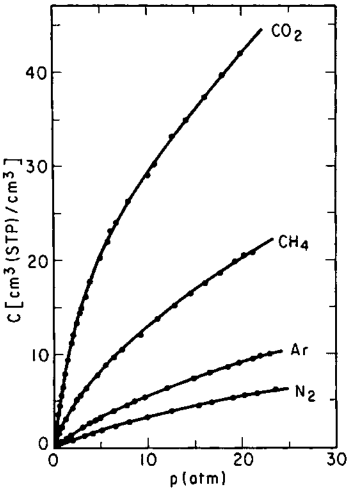

Fig. 1. Gas sorption isotherms at 35°C in poly(phenylene oxide).

Figure 3 demonstrates the quantitative agreement between the form of the $P(p_2)$ response for each gas and eq. (2). From these linear plots and the sorption parameters in Table II, the two diffusion coefficients, D_D and D_H, in the model were deduced for each gas, and the values found are given in Table III. In addition, the limiting permeabilities at high and low pressures are also tabulated. The permeation of helium was measured and its value is effectively independent of pressure. Since the solubility of helium is too low for accurate measurement, a diffusion coefficient for this gas was not obtained.

Comparison with Other Glassy Polymers

The Henry's law solubility coefficient for various gases in organic liquids has been found to correlate with the Lennard–Jones potential well-depth parameter, ϵ/k, for the gas in a manner described by the following equation[9]:

$$\log k_D = \log k_D^0 + m(\epsilon/k) \qquad (3)$$

Similar correlations have also been observed for gases in rubbery polymers.[1] Typical values[1] of the parameters k_D^0 and m from such correlations are given in Table IV. A thermodynamic rationalization for this relationship has been presented.[10] Interestingly, the empirical plots of log k_D vs. ϵ/k form a series of essentially parallel straight lines for a wide range of organic liquids and rubbery polymers. This implies that the slope m in eq. (3) is a constant independent of

TABLE II
Sorption Parameters for Poly(phenylene Oxide) at 35°C

Gas	k_D (cm³ (STP)/cm³·atm)	C'_H (cm³ (STP)/cm³)	b (atm⁻¹)
N_2	0.12	7.1	0.040
Ar	0.21	9.4	0.058
CH_4	0.33	18.1	0.11
CO_2	0.95	27.5	0.25

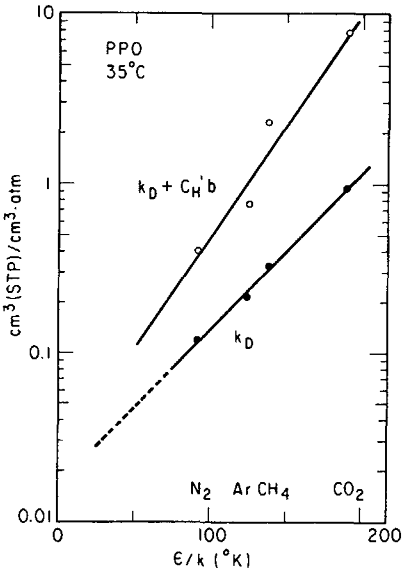

Fig. 2. Correlation of limiting slopes of sorption isotherms with the Lennard–Jones potential well-depth parameter.

the nature of the liquid or rubbery polymer while k_D^0 does depend on the nature of this phase. As shown in Table IV, m is of the order of 10^{-2} °K^{-1}, and k_D^0 varies somewhat depending on what the condensed phase is. Thus, a considerable base of experimental data for both low and high molecular weight fluids provide a useful empirical model for gas sorption against which observations for glassy polymers may be compared.

The limiting slopes of sorption isotherms at both high and low pressures for various gases in glassy polymers have also been shown to correlate in a similar manner with ϵ/k, and Figure 2 illustrates this for PPO. Values of m and k_D^0 for the limiting high pressure slope [k_D in terms of the dual sorption model expressed

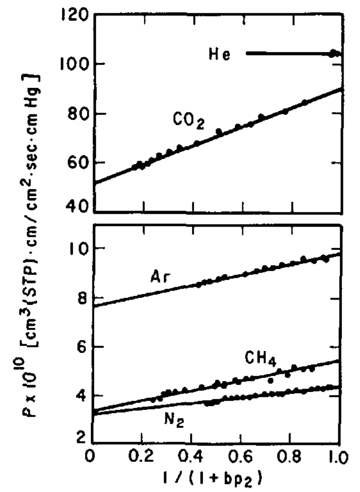

Fig. 3. Gas permeation data for poly(phenylene oxide) plotted according to eq. (2).

TABLE III
Transport Parameters for Poly(phenylene Oxide) at 35°C

Gas	$P(0)$	$P(\infty)$	D_D	D_H
He	—	110	—	—
CO_2	90.1	52.1	42.9	4.18
Ar	9.81	7.68	27.8	2.97
N_2	4.35	3.35	20.2	2.87
CH_4	5.45	3.39	7.81	0.786
Units	10^{-10} cm^3 (STP)·cm/cm^2·s·cm Hg		10^{-8} cm^2/s	

by eq. (1)] are also tabulated in Table IV for four glassy polymers including PPO. The values of m for glassy polymers are, within experimental certainty, identical with those for liquids and rubbers.

On the other hand, corresponding values for m computed using the low pressure slope of the sorption isotherm ($k_D + bC'_H$ in terms of the dual sorption model) are 50% or more larger than those shown. In an earlier publication,[11] it was shown for the CO_2—poly(ethylene terephthalate) system that the k_D parameter from the dual sorption model, obtained from sorption data below T_g, varied smoothly with temperature through the glass transition and formed a continuous connection with data above T_g, where simple Henry's law behavior was observed. The combination of these facts is strong evidence that the Henry's law term in eq. (1) is physically a manifestation of the same solubility mechanism operative in equilibrium condensed phases, viz., organic liquids or rubbery polymers. The values of k_D^0 for the glassy polymers form an entirely comparable range as those for rubbery polymers. The results of a recent study[5] imply that there may be a very slight but not large effect of molecular weight on this solubility mechanism. It is clear from Table IV that the Henry's law part of gas sorption in PPO is within the range observed for other polymers.

If the Henry's law portion of eq. (1) stems from an equilibrium sorption mechanism as argued above, then it follows that the Langmuir part probably is the result of the nonequilibrium character of the glassy state. The latter point was suggested earlier and is supported by considerable evidence.[1,5–8,11–15] Ad-

TABLE IV
Typical Parameters for Correlation $\log k_D = m(\epsilon/k) + \log k_D^0$ Characterizing Gas Solubility in Various Amorphous Materials

	Material	m × 10^2 (°K^{-1})	$k_D^0 \times 10^2$ (cm^3 (STP)/cm^3·atm)	T (°C)
Liquids:	Benzene	0.95	2.98	25
	n-heptane	0.94	1.69	25
Rubbers:	Natural rubber	0.94	1.11	25
	Silicone rubber	0.94	1.88	25
	Butyl rubber	1.00	0.90	25
	Amorphous polyethylene	0.94	0.72	25
	Polychloroprene	0.97	1.10	25
Glasses:	Polycarbonate	0.92	1.15	35
	Polysulfone	0.96	0.93	35
	Copolyester	0.96	1.03	35
	Poly(phenylene oxide)	0.93	1.65	35

ditional evidence for this can be seen by examining the Langmuir capacity C'_H for one gas, CO_2, measured at a single temperature of 35°C in a wide range of glassy polymers. Figure 4 shows C'_H plotted vs. their glass transition temperatures. A remarkable correlation exists among these many different polymers. As suggested by the line drawn visually through these data, the Langmuir term would not exist for a polymer with T_g below the observation temperature of 35°C, i.e., for a rubbery polymer, but its capacity grows steadily as the T_g increases above this limit. In a very straightforward manner this indicates that the exceptionally large solubility of gases in PPO stems from its high T_g and its effect on the Langmuir mode of sorption.

It was proposed earlier[1,5–8,11–14] that the Langmuir term arises from packing of gases like CO_2 into the unrelaxed volume of the glass ($V_g - V_l$) with a liquidlike density. The unrelaxed volume at any temperature T may be estimated from thermal expansion coefficients above and below T_g; i.e.,

$$\frac{V_g - V_l}{V_g} = (\alpha_l - \alpha_g)(T_g - T) \tag{4}$$

Since ($\alpha_l - \alpha_g$) values are quite similar for most polymers,[16] it follows from this picture that C'_H should be proportional to ($T_g - T$), as seen in Figure 4. The only support for this interpretation of the Langmuir mode is the quantitative agreement with it shown by numerous sets of experimental observations. Although Figure 4 is likewise consistent with this interpretation, these observations are in no way limited by its validity since this presentation is entirely phenomenological.

The permeability coefficient given by eq. (2) reduces in the limit of high pressure to a form similar to the familiar expression for rubbery polymers, which is the product of solubility and diffusion coefficients. The former coefficient depends on the condensibility of the gas as expressed by eq. (3) while the latter depends on the size of the gas molecule.[6–8] For a limited range of simple gases like those employed here, the composite coefficient for permeability can be represented as a function of the molecular diameter of the gas determined from zeolite sorption,[6] as shown in Figure 5. Such a plot will break down for more

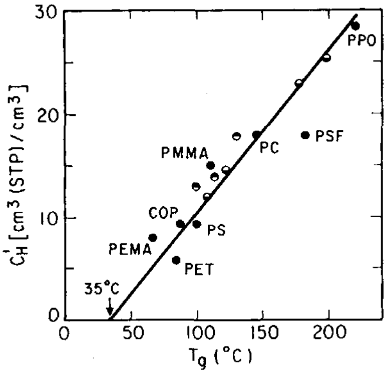

Fig. 4. Correlation of measured values of the Langmuir sorption capacity at 35°C with the glass transition temperature of the polymer. PPO = poly(phenylene oxide), PSF = polysulfone, PC = polycarbonate, PMMA = poly(methyl methacrylate), PS = polystyrene, COP = a copolyester (see Ref. 8), PEMA = poly(ethyl methacrylate), and PET = poly(ethylene terephthalate). Miscible blends of polymer pairs shown: (◒) PPO/PS; (◓) PC/COP.

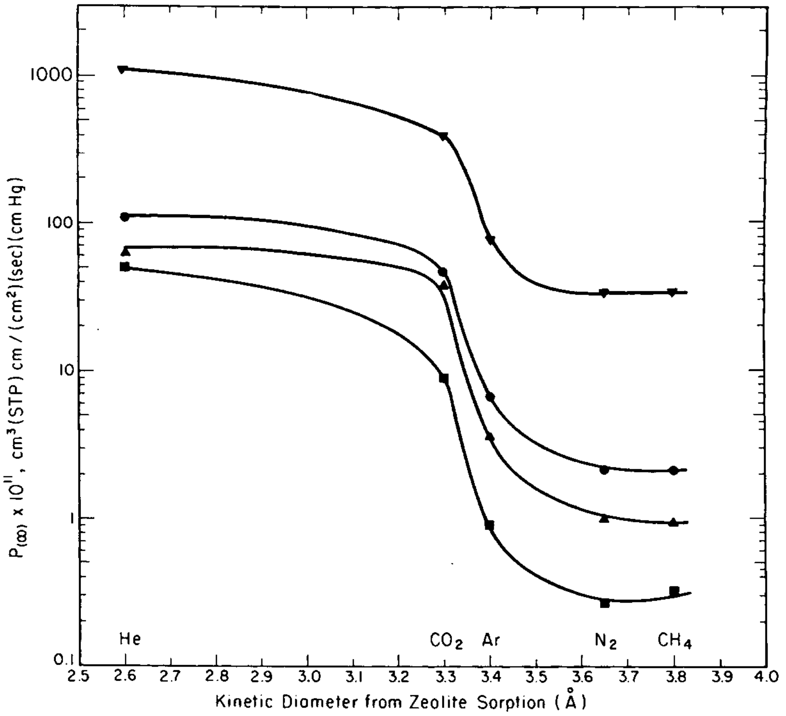

Fig. 5. Permeability coefficients at 35°C for four glassy polymers vs. the molecular diameter of the gas molecule: (▼) PPO; (●) polycarbonate; (▲) polysulfone; (■) copolyester; $\lim_{p_2 \to \infty} P = P(\infty) = k_D D$.

complex gases, but this limited correlation forms a useful presentation for present purposes. PPO is clearly the most permeable to all gases of the four glassy polymers compared here. Each of these polymers has aromatic units in the backbone of the chain, and their glass transitions range from a low of 87°C for the copolyester[8] to a high of 220°C for PPO. As seen in Table IV, differences in the Henry's law solubility coefficients among these polymers are not very great and cannot account for the large differences in permeabilities seen. The permeabilities for the two extremes, PPO and copolyester, lie approximately two decades apart, most of which stems from the much larger diffusion coefficients for gases in PPO. At present, there is no simple way to rationalize the variation in diffusion coefficients among these polymers.

Table III summarizes for PPO the diffusion coefficients for the Henry's law and Langmuir populations, D_D and D_H, respectively. Both decrease as the effective diameter of the gas molecules increase as found for the other three polymers.[6–8] Earlier,[8] it was suggested that the ratio of the two diffusion coefficients, F, decreases as the Lennard–Jones potential well-depth parameter for the gas increases. Figure 6 extends the presentation of this suggestion by adding the results for PPO which roughly fit this trend. An intriguing fact emerges from Figure 6, and this is that the ratio F is smaller for those polymers with larger permeabilities or diffusion coefficients. Stated another way, the gas molecules sorbed by the Langmuir mode are relatively more immobilized in PPO than they

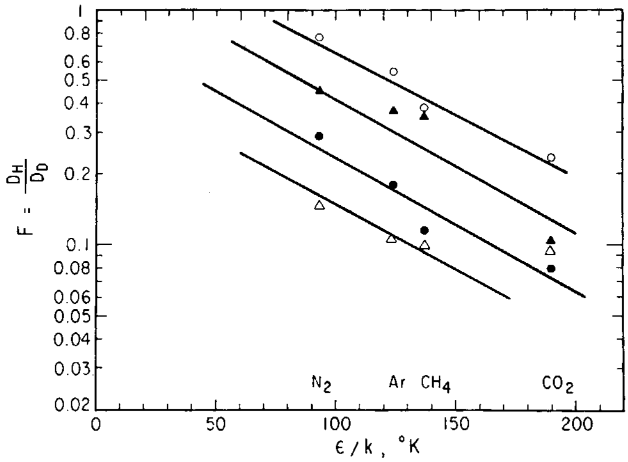

Fig. 6. Ratio of Langmuir to Henry's law diffusion coefficients for four glassy polymers correlated with the Lennard–Jones potential well-depth parameter: (○) copolyester; (▲) polysulfone; (●) polycarbonate; (△) PPO.

are in the copolyester. The latter observation raises the question of what general relationship may exist between the two diffusion coefficients D_H and D_D. One approach to this is to plot D_H vs. D_D for the various gas–polymer combinations which have been studied to date by our laboratory, and this has been done in Figure 7. As one might expect, there is no unique relation between the two coefficients, but interestingly there is a general trend among the results. Apparently, the mobilities of the molecules held by the two sorption modes are influenced to a certain degree by the same factors of gas and polymer structure.

According to the premises of the dual sorption/transport models and the interpretations advanced above, the nonequilibrium character of glassy polymers contributes an additional mechanism to gas permeation in parallel to the normal

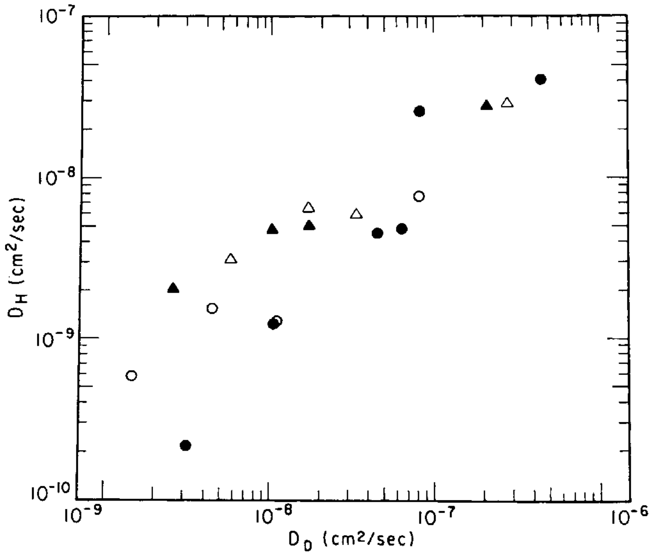

Fig. 7. Empirical plot of Langmuir mode diffusivity vs. the Henry's law mode diffusivity for numerous polymer–gas pairs: (●) CO_2; (△) Ar; (▲) N_2; (○) CH_4.

processes expected from its equilibrium character. It is interesting to examine how large this contribution might be for various polymers. At high pressures this contribution is zero since from eq. (2)

$$P(\infty) = k_D D_D \tag{5}$$

while at very low pressures its effect is at a maximum

$$P(0) = k_D D_D + C'_H b D_H \tag{6}$$

or

$$\frac{P(0)}{P(\infty)} = 1 + \frac{C'_H b}{k_D} \frac{D_H}{D_D} \tag{7}$$

For CO_2, the ratio $P(0)/P(\infty)$ for PPO is 1.73 while for the copolyester it is 1.55. Interestingly, these two ratios are rather similar because of compensating effects between solubility and transport effects—PPO has a high value of C'_H but a low F while the copolyester has a lower C'_H but a larger F.

SUMMARY

Sorption and permeation results for various gases in PPO are well described by the dual sorption and transport models which have been employed successfully for other glassy polymers. The very large gas solubilities observed for PPO are a result of the high glass transition temperature of this polymer which leads to a large Langmuir sorption capacity. This large solubility, however, is only a minor factor in the large gas permeabilities exhibited by this polymer. The latter stems from the larger diffusion coefficients of gases in PPO compared to others, which widely reflects some measure of the state of packing of the chains.

This research was carried out with financial support of the National Science Foundation, Grants DMR 74-01534-AO2 and DMR 80-01665, Polymer Program.

References

1. D. R. Paul, *Ber. Bunsenges Phys. Chem.*, **83,** 294 (1979).
2. J. T. Koberstein and S. L. Cooper, *Rev. Sci. Instrum.*, **46,** 1639 (1975).
3. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci., Polym. Phys. Ed.*, **14,** 687 (1976).
4. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **14,** 1903 (1976).
5. K. Toi and D. R. Paul, *Macromolecules*, to appear.
6. W. J. Koros, A. H. Chan and D. R. Paul, *J. Membr. Sci.*, **2,** 165 (1977).
7. A. J. Erb and D. R. Paul, *J. Membr. Sci.*, **8,** 11 (1981).
8. P. Masi, D. R. Paul, and J. W. Barlow, *J. Polym. Sci., Polym. Phys. Ed.*, **20,** 15 (1982).
9. J. H. Hildebrand and R. L. Scott, *Regular Solutions*, Prentice-Hall, Englewood Cliffs, N.J., 1962, Chap. 4.
10. T. K. Kwei and W. M. Arnheim, *J. Polym. Sci.*, **2A,** 1873 (1964).
11. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **16,** 1947 (1978).
12. A. H. Chan and D. R. Paul, *Polym. Eng. Sci.*, **20,** 87 (1980).
13. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5,** 63 (1979).
14. G. Morel and D. R. Paul, *J. Membr. Sci.*, to appear.
15. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **19,** 1655 (1981).
16. S. C. Sharma, L. Mandelkern, and F. C. Stehling, *Polym. Lett.*, **10,** 345 (1972).

Received December 15, 1981
Accepted January 25, 1982