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REPEAT UNIT STRUCTURE AND GAS TRANSPORT PROPERTIES OF AROMATIC POLYMERS

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ABSTRACT

Structure/transport-property correlations for a family of aromatic polyesters and polyphenylene oxides are presented. How modification in repeat unit structure changes the packing of bulk polymers, and subsequently the solubility and diffusivity of gases in polymers is addressed in detail. In addition to polymer-gas attraction, polymer packing density is proposed to be an important factor in determining the gas-absorbing capacity of glassy polymers. The observed diffusivity data are strongly correlated with polymer packing. Moreover, scatter in the correlation can be satisfactorily attributed to differences in local chain mobility among the polymers investigated here.

INTRODUCTION

Transport of gases in nonporous glassy polymers is generally accepted to obey the solution-diffusion mechanism. Therefore, in studies dealing with structure-property correlations, solubility and diffusivity considerations should be addressed separately. From a material point of view, of major concern is how changes in chemical make-up of the polymer repeat unit influence the solubility and diffusivity of penetrants in the polymer(1).

Diffusivity and solubility values of different gases in a given polymer are generally accepted to depend predominantly on size, shape and condensability of the gases, and to a lesser extent, on attraction between the gases and the polymer. On the other hand, no consensus exists regarding factors controlling the diffusivity and solubility of a given gas in different polymers. For simplicity, we will assume that packing density and local chain mobility of the polymers are the major parameters which determine the transport rate of a given gas in different glassy polymers. Conventionally, packing density of a polymer has not been considered as a factor which may influence the polymer's gas-sorbing capacity. But based on our studies on brominated PPOs(2, 3), we found that packing density may be important in determining the ability of polymer to absorb gases. These hypotheses are summarized in Table 1.

In this paper, we will address how packing density and local chain mobility are altered by structural variation in the polymer repeat unit, and present subsequent changes in solubility and diffusivity of the individual gases. The polymer repeat units covered here are listed in Figure 1. Clearly, these polymers are either aromatic polyethers or aromatic polyesters. Nevertheless, their properties vary over a reasonably wide range such that some generalizations can be made from conclusions derived from these systems.

Table 1 Proposed structure-property relationships

	Properties of the Polymer	Properties of the Gas
Diffusivity	Packing density Local chain mobility	Size and Shape
	Polymer-Gas attraction	
Solubility	Packing density	Condensability

EXPERIMENTAL

Materials

All the gases, greater than 99% pure as supplied by the vendors, were used without further purification. The polymers were either synthesized or chemically modified in this laboratory(4, 5).

Sorption and Permeation Measurements

Steady-state permeability to pure gases was measured with a barometric type of device where the pressure in a known downstream volume is monitored as the gas permeates through the film and accumulates in the downstream volume(6). The downstream pressure was kept below 10 mmHg and the upstream pressure was varied. Sorption isotherms of the pure gases were measured with a dual transducer barometric device(7). Detailed procedures for the construction, operation, and calibration of the apparatus can be found in the literature(8).

RESULTS AND DISCUSSION

Packing Density

Mass density(1, 9), d-spacing from x-ray diffraction(10), and specific empty volume(11) all have been used for ranking the packing density of polymers. However, we consider the following parameter(2) more appropriate:

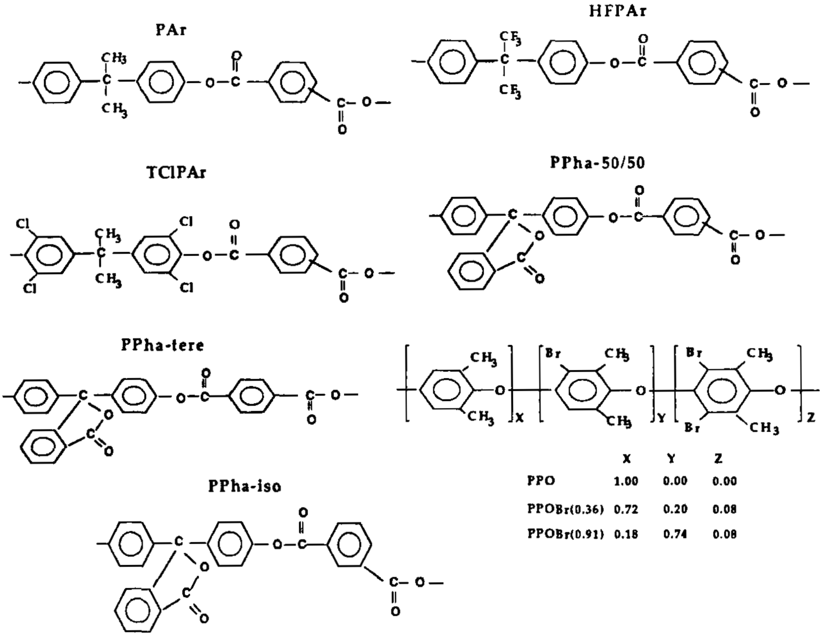
$$1/V_f = \text{specific volume}/(\text{specific volume} - \text{specific van der Waals volume})$$

The specific volume is determined experimentally from density measurement (typically with a density gradient column at 23°C). The specific van der Waals volume is calculated from the group contribution method reported by Bondi(12). Clearly, a larger $1/V_f$ value corresponds to a larger packing density. (The value of $1/V_f$ will change slightly if density data at other temperatures are used.)

Table 2 is a summary of the packing densities of the polymers listed in Figure 1. Several observations can be made from the data in Table 1.

First, taking PPO as the reference, one finds that aryl-bromination of PPO significantly lowers packing density. Similarly, the packing density of TClPAr is less than that of PAr. Aryl-halogenation therefore appears to be an effective modification for reducing the packing density of at least these two types of polymers. These results are consistent with literature data for aryl-methylated and aryl-halogenated bisphenol A polycarbonates(13-15).

Second, comparing HFPAr with PAr, one finds that HFPAr has a lower packing than PAr. This observation is consistent with literature data on their polycarbonate counterparts(13-15), PC and HFPC. Presumably, the large size and rigidity of $-CF_3$ relative to $-CH_3$ cause the observed reduction in packing in both cases.



	X	Y	Z
PPO	1.00	0.00	0.00
PPOBr(0.36)	0.72	0.20	0.08
PPOBr(0.91)	0.18	0.74	0.08

Figure 1 Repeat unit structures of the polymers

Table 2. Calculated packing density and solubility parameter

Polymers	Density g/cm^3	$1/V_f$	Solubility Parameter [a] $(cal/cm^3)^{0.5}$
PPO	1.061	2.55	9.6
PPOBr(0.36)	1.203	2.47	9.5
PPOBr(0.91)	1.380	2.38	9.4
PPha-iso	1.304	2.80	11.0
PPha-50/50	1.298	2.79	11.0
PPha-tere	1.297	2.78	11.0
TCl PAr	1.368	2.70	10.0
HFPAr	1.418	2.67	9.4
PAr	1.204	2.77	10.3

[a] Calculated values (Hoy, K. L., 1970, J. Paint Technology).

Third, comparing PPha-50/50 with PAr, one must conclude that introduction of a polar "cardo" group does not significantly change the packing density of the polymer. This somewhat unexpected ineffectiveness of phenolphthalein in reducing the packing density may be related to additional interchain attraction between the cardo ester groups in phenolphthalein, which counteracts the would-be reduction in packing due to steric effect alone. The fact that HFPAr and HFPC do exhibit lower packings than their respective hydrogenated counterparts appears to support this hypothesis since fluorination is not expected to significantly increase interchain attraction.

Solubility

The sorption solubilities of carbon dioxide, methane and nitrogen at 35°C are presented in Figures 2(a), 2(b), and 2(c). Clearly, PPO and its aryl-brominated derivatives absorb slightly less carbon dioxide than the polyesters do (except PAr). But the PPOs absorb significantly more methane and nitrogen than the polyesters.

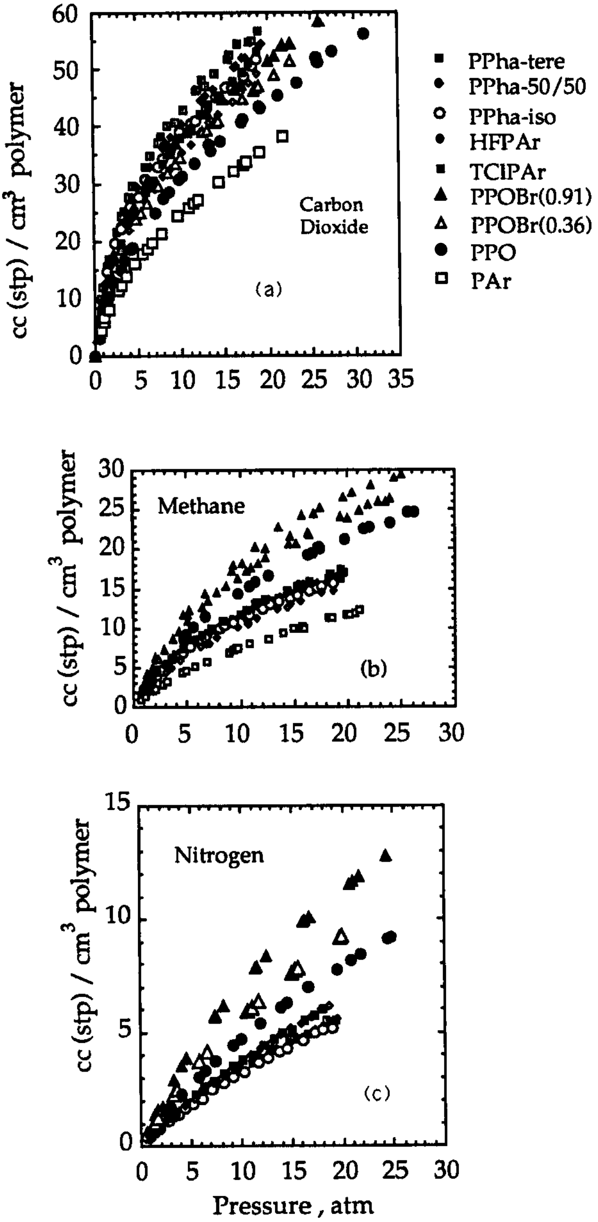


Figure 2 Equilibrium sorption isotherms at 35°C.

Obviously, there is no apparent correlation between calculated polymer solubility parameter (Table 2) and the solubility data. Following the hypotheses presented in Table 1, one may attribute the large sorption capacity of PPOs for all three gases to their low packing densities relative to the polyesters. That the polyesters absorb more carbon dioxide but less methane and nitrogen than the PPOs presumably is due to preferable attraction between carbon dioxide, but not the other two gases, and the ester groups(16).

Alternatively, following the formalism of the dual-mode model(17), one may establish similar polymer correlations between gas solubility and polymer repeat-unit structure. Table 3 summarizes the relative dual-mode sorption parameters k_D and C_H' of carbon dioxide, nitrogen and methane. The parameters were obtained from a non-linear regression analysis on the sorption isotherm according to the following dual-mode model equation(7, 8):

$$C = k_D p + \frac{C'_H bp}{1 + bp} \qquad [1]$$

where C is gas solubility in polymer, cc(stp)/cm^3 polymer
k_D is Henry's law constant, cc(stp)/cm^3 polymer-atm
b is Langmuir affinity constant, 1/atm
C_H' is Langmuir sorption capacity, cc(stp)/cm^3 polymer, and
p is gas pressure, atm

Clearly, the Henry's law constant k_D of either methane or nitrogen varies only over a narrow range among the nine polymers. In contrast, the Langmuir constant C_H' of either gas in the PPOs is distinctly larger than that in the polyesters, presumably reflecting the contribution of lower packing density. On the other hand, the Langmuir capacities for carbon dioxide of either group of polymers are comparable but the k_D's of carbon dioxide in the polyesters are larger, suggesting additional attraction between the esters and carbon dioxide.

Lower packing also appears to decrease the "solubility-selectivity" of the polymer as reflected in the data in Table 4. The values presented are for a gas pressure of 10 atm. It should be noted that the following discussion is insensitive to the gas pressure at which data are evaluated.

Table 3 Relative dual-mode sorption parameters. The parameter values of PPO are designated to be 1.

Polymers	Gases					
	CH_4		N_2		CO_2	
	k_D	C_H'	k_D	C_H'	k_D	C_H'
PPO	1.00	1.00	1.00	1.00	1.00	1.00
PPOBr(0.36)	1.07	1.12	1.05	1.19	1.02	1.08
PPOBr(0.91)	1.18	1.21	1.08	1.51	1.05	1.15
PPha-iso	1.02	0.58	1.03	0.41	1.33	0.96
PPha-50/50	1.01	0.62	0.99	0.44	1.34	1.06
PPha-tere	1.00	0.62	1.01	0.47	1.42	1.11
TClPAr	1.00	0.70	1.18	0.56	1.57	0.89
HFPAr	1.03	0.56	1.28	0.56	1.40	0.87
PAr	0.85	0.40	-----	-----	1.06	0.60

Table 4 Correlation between "solubility--selectivity" and packing density.

Polymers	$1/V_f$	S_{CH_4}/S_{N_2} [a]	S_{CO_2}/C_{CH_4}
PPO	2.55	3.08	2.10
PPOBr(0.36)	2.47	2.92	2.08
PPOBr(0.91)	2.38	2.60	2.03
PPha-iso	2.80	3.48	3.41
PPha-50/50	2.79	3.38	3.47
PPha-tere	2.78	3.45	3.63
TClPAr	2.70	3.21	3.09
HFPAr	2.67	2.76	3.42

[a] S_i is the apparent solubility coefficient of gas i, evaluated from the secant slope of the sorption equilibrium isotherm at 10 atm (Figure 3).

The solubility ratios of methane to nitrogen of the PPOs are clearly less than those of the polyesters. (Both gases are not expected to interact favorably with either type of polymers). Moreover, among the PPOs the same ratio decreases from PPO to PPOBr(0.36) to PPOBr(0.91). These trends are consistent with the order of decreasing packing densities of the polymers. The remarkably lower CO_2/CH_4 solubility-selectivity of the PPOs is presumably due to the combined effects of PPO's lower packing and lack of favorable attraction with carbon dioxide.

Diffusivity

Assuming that Fickian diffusion and solution-diffusion mechanism are applicable, one can determine the diffusion coefficient from steady-state permeability and equilibrium sorption data. In the following analysis, the dual-mode partial immobilization model will be used. It should be noted that similar conclusions can be obtained even if one chooses not to apply any particular model and uses concentration-dependent "apparent diffusivity" in the discussion.

According to the dual-mode model, the steady-state permeability, P, for a case where the upstream and downstream pressures are maintained at p and zero, respectively, can be written as(18):

$$P = k_D D_D \left(1 + \frac{\frac{D_H}{D_D} \cdot K}{1 + bp}\right) \qquad [2]$$

where $K = C_H'b/k_D$, D_D = Henry's mode diffusion coefficient

D_H = Langmuir mode diffusion coefficient

The values of D_D and D_H can be determined once the steady-state permeability and equilibrium sorption data are available.

Presented in Table 5 are the diffusivity data for carbon dioxide, methane, and nitrogen. Clearly, the D_D value changes over an order of magnitude, but the "diffusivity-selectivity", both $(D_D)_{CO_2}/(D_D)_{CH_4}$ and $(D_D)_{CH_4}/(D_D)_{N_2}$ are relatively constant. (Similar statement can be made for D_H ratios except that they vary over a larger range because of the larger uncertainty in the individual D_H' values.)

We had hypothesized in Table 1 that packing density and local chain motion of polymer control the diffusivity of gas inside the polymer.

This hypothesis can be tested by plotting D_D versus the packing density as shown in Figure 3(a) to 3(c). Additional data for other polymers found in the literature are also included in the figures. Clearly, there is a strong correlation between polymer packing density and gas diffusivity in the polymer. Moreover, polymers with aryl-substitutions, which presumably have less local chain mobility(19, 20), tend to exhibit lower gas-diffusivity as indicated by the lower straight line arbitrarily drawn in Figures 3(a) to 3(c). Incorporating the data for polyacrylonitrile(6), poly(1-trimethylsilyl-1-propyne)(21), and Kapton polyimide(22), one can expand the correlation over a much wider diffusivity values, such as shown in Figure 4 for carbon dioxide. Note that the point for PAN falls on the low side of the correlation, which could be attributed to diminished local chain mobility because of the strong attraction between -C ≡ N groups.

The combined effects of packing density and local chain mobility is manifested even more vividly in the gas-diffusivity of the three polymeric "isomers", PPha-iso, PPha-50/50, and PPha-tere. (Literature data(23, 24) on the permeability of polymeric isomers containing isophthalic and terephthalic entities can also be interpreted satisfactorily with the following analysis). The solubilities of pure carbon dioxide, methane, and nitrogen in these three polymers are comparable (Figure 2), but PPha-tere is over 100% more permeable to gases than PPha-iso(5), reflecting a large difference in the values of diffusivity (Table 5). The small gas-diffusivity in PPha-iso relative to that in PPha-tere can be attributed to the larger packing density (Table 2) and lesser local chain mobility of PPha-iso.

The observations discussed in the last three paragraphs strongly suggest that by reducing the packing density of the polymer, one can effectively increase the diffusivity of gas in polymer. Over a certain range of packing densities the increase in gas-diffusivity can be accomplished without much change in "diffusivity-selectivity" for mixtures of at least nitrogen, methane and carbon dioxide. Actually, concurrent reduction in local chain mobility together with packing reduction, such as by aryl-substitution, tends to increase the "diffusivity-selectivity", though not considerably, at the same time when gas-diffusivity is increased, as shown by comparison among the PPOs and between PAr and TClPAr.

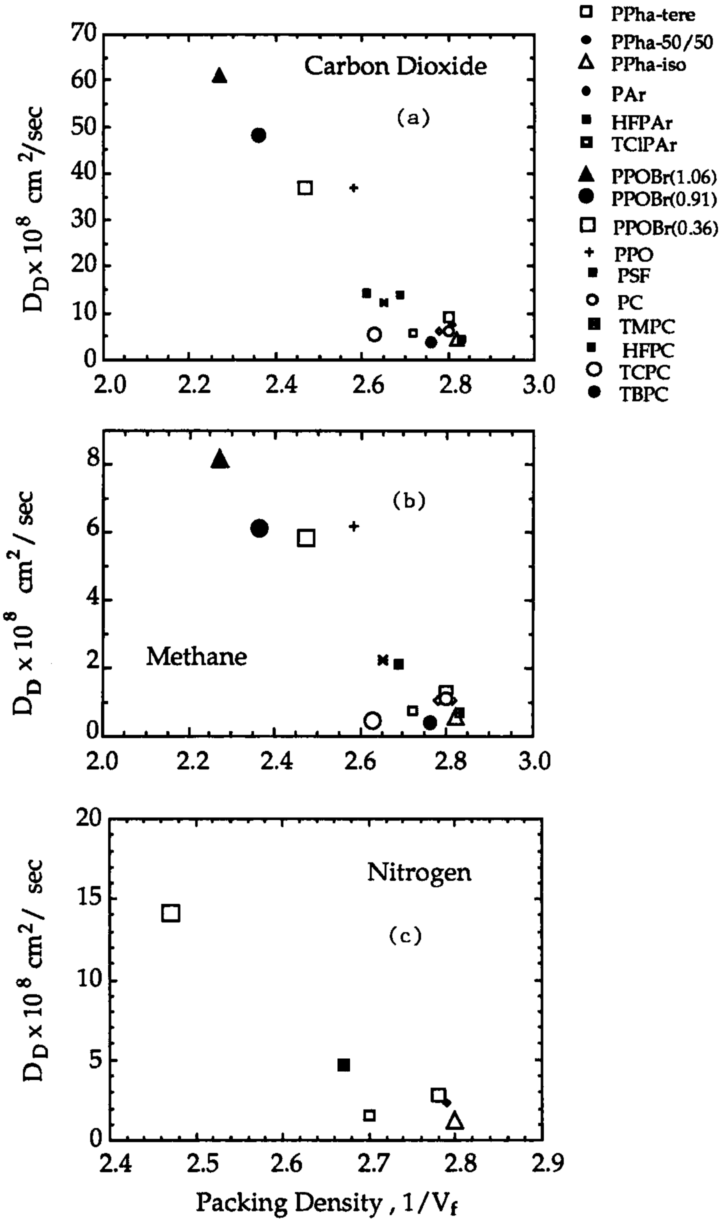


Figure 3 Correlations between D_D and polymer packing density, $1/V_f$. 35°C

Table 5 Dual-mode diffusion coefficients. D_D : $10^{-8}cm^2/s$, D_H : $10^{-9}cm^2/s$

Polymers	Gases						Diffusivity Ratios	
	CO_2		CH_4		N_2		$\frac{(D_D)_{CO_2}}{(D_D)_{CH_4}}$	$\frac{(D_D)_{CH_4}}{(D_D)_{N_2}}$
	D_D	D_H	D_D	D_H	D_D	D_H		
PPO	36.8	36.8	6.2	4.3	_ _	_ _	5.9	_ _
PPOBr(0.36)	36.9	26.9	5.8	3.2	14.1	2.82	6.4	0.41
PPOBr(0.91)	48.2	33.0	6.1	2.9	_ _	_ _	7.9	_ _
PPha-iso	4.44	2.22	0.56	0.40	1.30	0.94	7.9	0.43
PPha-50/50	7.65	5.73	1.03	0.82	2.33	1.52	7.4	0.44
PPha-tere	9.24	5.75	1.31	1.14	2.81	2.16	7.0	0.47
TClPAr	5.81[a]	_ _ _	0.77	0.71	1.59	1.97	7.0	0.48
HFPAr	12.98	10.0	2.04	1.68	4.66	5.21	6.4	0.44
PAr	6.15	5.49	1.04	0.90	_ _	_ _	5.9	_ _

[a] Because of CO_2-induced plasticization, this value is estimated from data collected at low pressures.

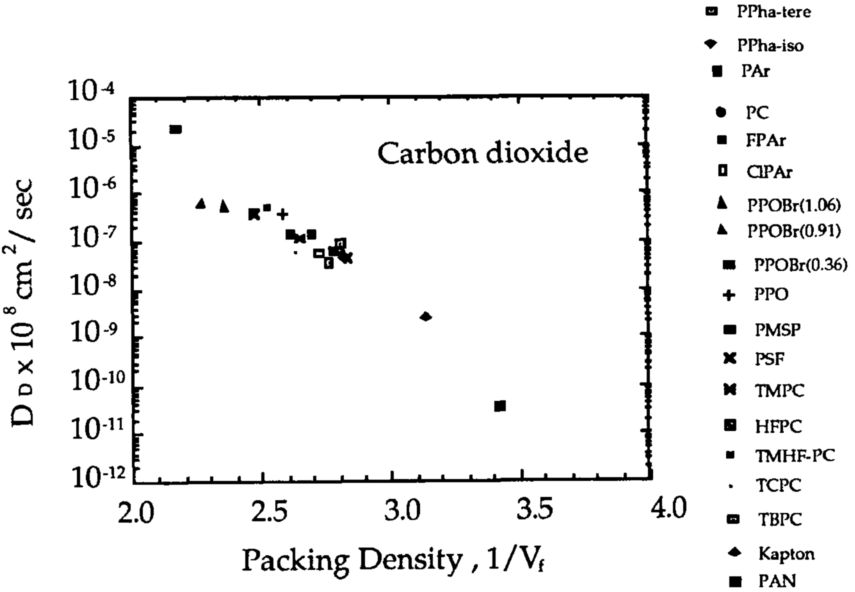


Figure 4 Extended correlation between D_D and packing density

CONCLUSIONS

Aryl-substitution was shown to be an effective way for reducing the packing density of glassy aromatic polymers. Substituting the isopropylidene entity in bisphenol A with its perfluorinated counterpart also reduces the packing density of the polyester. However, exchanging the isopropylidene with an at least equally bulky "cardo" group (in phenolphthalein) does not decrease the packing density, presumably due to counteracting effects of increased interchain attraction between the polar ester groups.

In addition to gas-polymer attraction, packing density has an apparent effect on the gas-sorbing capacity of polymer. The sorption-selectivity of polymer for non-interacting gases, methane and nitrogen (S_{CH_4}/S_{N_2}) also appears to diminish with decreasing packing density.

Gas diffusivity in polymer was found to correlate very strongly with polymer packing density. The correlation remains reasonable even when the glassy polymeric barrier, polyacrylonitrile, and the most permeable (glassy) polymer, poly(1-trimethylsilyl-1-propyne) are incorporated (Figure 4); which covers five orders of magnitude of diffusivity values. Moreover, much of the scatter in the correlation can be accounted for qualitatively by considering local chain mobility which conventionally has been inferred from sub-Tg dynamic relaxation data. The causes for lesser local chain mobility can be either steric factors (e.g. by aryl-halogenation), configuration (e.g. iso- relative to tere- phthalate), or unusually strong interchain attractions (e.g. in PAN).

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