

Gas permeation in polyarylates: effect of bisphenol and acid substitution symmetry

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The effect of bisphenol substitution symmetry on gas permeation as well as other relevant structural properties of polyarylates has been investigated both experimentally and by molecular modelling. Asymmetric or di-substitution of methyl groups on the phenyl rings of bisphenol-A or phenolphthalein resulted in polyarylates with similar packing density and permeability and with increased permselectivity compared to the corresponding polymers with the unsubstituted bisphenols. Symmetric or tetra-substitution of methyl groups on the bisphenol-A phenyl rings led to polyarylates with decreased packing density, increased permeability and similar selectivities as the corresponding polymers with the unsubstituted bisphenol. Molecular modelling studies of the chain conformation gave further insight into the mechanism by which substitution symmetry affects the polymer properties. The differences in the minimum energy chain conformation of symmetrically and asymmetrically substituted bisphenol-A polyarylate chains help in explaining the variation in packing density and permeation properties. Calculations of relative bond flexibility and the energy barrier for bond rotation of specific moieties in the minimized energy chain conformation correlate with molecular mobility as measured by sub- T_g transition temperatures. The diacid used for polyarylate synthesis was also varied in order to investigate the effect of acid linkage symmetry. Polyarylates based on the above bisphenols and asymmetrically linked isophthalic acid were compared with the corresponding polymers based on symmetrically linked terephthalic acid or 2,6-naphthalene dicarboxylic acid. Isophthalic acid-based polyarylates had higher packing density, chain mobility, and permselectivity and lower permeability than their terephthalic acid-based counterparts. Incorporation of the naphthalene acid along with the terephthalic acid also results in polyarylates with lower packing density and higher chain rigidity than the isophthalic acid-based polymers. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

As reviewed by Koros and Fleming¹ and Stern², systematic studies of structural variation in various families of glassy polymers can lead to superior permeation characteristics. Substitution at the bridge or ring carbon of the bisphenol moiety has been shown to affect permeation characteristics in polycarbonates^{3,4}, polyarylates^{5,6} and polysulfones⁷.

Symmetric or tetramethyl substitution on the bisphenol-A phenyl rings has been shown to lead to higher permeabilities in polysulfone⁷, polycarbonate⁴ and polyarylate⁶ with similar or slightly reduced selectivities. Asymmetric or dimethyl substitution is known to reduce permeability with increased selectivity in polysulfone⁷, polycarbonate³ and polyarylate⁶. A previous molecular modelling study⁸ of bisphenol-A-based polyarylates has shown a major role for the bisphenol moiety in determining chain conformation and rigidity. Since the trend in permeation properties with methyl group substitution symmetry appears to hold in several glassy polymers, it is of interest to examine the reasons for this behaviour.

In the present study, we have examined bisphenol phenyl ring substitution symmetry along with acid linkage

symmetry in various polyarylates. The issue of symmetric *versus* asymmetric bisphenol phenyl ring substitution is first discussed by comparing the permeation and physical properties of polyarylates based on bisphenol-A, dimethyl-bisphenol-A and tetramethyl bisphenol-A with the symmetrically (para) linked terephthalic acid. Molecular modelling is used to identify the role of various moieties in the polymer chain on its conformation and flexibility. This information can be used to understand effects of symmetric or asymmetric substitution on physical parameters such as packing density and chain/subgroup rigidity which are known to affect permeation properties. These effects of bisphenol phenyl ring substitution are then examined in polyarylates incorporating the asymmetrically (meta) linked isophthalic acid. Polyarylates based on symmetrically linked 2,6-naphthalenedicarboxylic acid were examined in order to see the effect of increased rigidity coupled with symmetric acid linkage.

EXPERIMENTAL

Monomers

Tetramethylbisphenol-A (TMbisA) and dimethylbisphenol-A (DMbisA) were prepared by the acid catalysed condensation of 2,6-dimethylphenol or *o*-cresol, respectively, with acetone according to the procedure of

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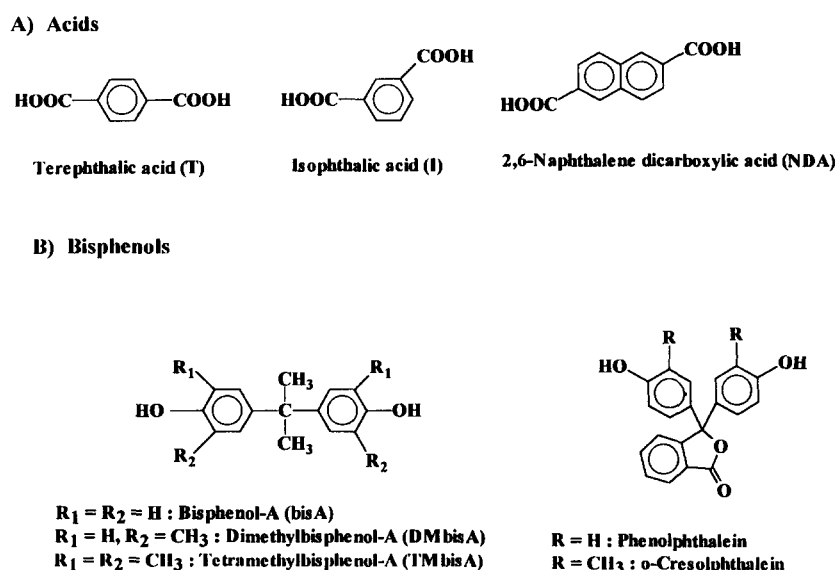


Figure 1 Structure of the monomers used in the present work

Table 1 Identification of polymers studied in the present work

Polymer name	Monomers used in the polymer synthesis	
	Bisphenol	Acid/mixture of acids in molar equivalents
BisA-T	BisA	T
BisA-I + T	BisA	I(50) + T(50)
BisA-I	BisA	I
DMbisA-T	DMbisA	T
DMbisA-I + T	DMbisA	I(50) + T(50)
DMbisA-I	DMbisA	I
TMbisA-T	TMbisA	T
TMbisA-I + T	TMbisA	I(50) + T(50)
TMbisA-I	TMbisA	I
BisA-NDA(80) + T(20)	BisA	NDA(80) + T(20)
DMbisA-NDA(80) + T(20)	DMbisA	NDA(80) + T(20)
TMbisA-NDA(80) + T(20)	TMbisA	NDA(80) + T(20)

Venkateswara *et al.*⁹ *o*-Cresolphthalein (*o*-Cp) was obtained from M/s. Aldrich Chemicals, USA and purified by repeated recrystallization in acetic acid:water mixture. Isophthalic acid (I) was procured from M/s. SRL India while terephthalic acid (T) and 2,6-naphthalene dicarboxylic acid (NDA) were procured from M/s. Aldrich Chemicals, USA. These dicarboxylic acids were used without further purification. Acid chlorides were obtained by refluxing the respective acids in 4 M equivalents of thionyl chloride using *N,N*-dimethyl formamide as the catalyst. Iso- and terephthaloyl dichlorides were purified by recrystallization in petroleum ether; while 2,6-naphthalene dicarbonyl dichloride was recrystallized from a toluene:petroleum ether mixture. Benzyltriethylammonium chloride (BTEAC) was obtained from M/s Fluka, Switzerland.

The monomer structure and abbreviation used in the present study are given in *Figure 1*.

Polymer synthesis

The polymers are denoted by the starting monomer abbreviations (see *Table 1* and *Figure 1*). All the polymers were synthesized by interfacial polymerization. In a typical procedure, 5 mmol of bisphenol was dissolved in 10 ml aqueous solution of NaOH (0.42 g NaOH, 10.5 mmol, 2.1 equivalents) with stirring and further diluted to 50 ml. 28.5 mg (0.125 mmol, 0.025 equivalents) of benzyltriethy-

lammonium chloride was added to the solution as a phase transfer catalyst. 20 ml of CH_2Cl_2 was then added as an organic phase and the mixture was vigorously stirred at 2000 rpm. 5.25 mmol (1.05 equivalents) of acid chloride(s) was dissolved in 5 ml of CH_2Cl_2 and the solution added dropwise to the above vigorously stirred emulsion containing bisphenol over a period of 10 min. In the case of NDA containing copolymers, this addition time was extended up to 30 min in order to avoid either T or NDA block formation. The mixture was stirred continuously for 1 h and then allowed to separate. The aqueous layer was discarded and the organic layer was added slowly to 500 ml of methanol in a stirred beaker. The precipitated polymer was first dried in an oven at 50°C and residual solvents were removed in vacuum at 60°C. All polymers were finally purified by dissolving in either $CHCl_3$ or *sym*-TCE, followed by precipitation in either acetone or methanol.

The polymers were characterized for various physical properties of interest which are summarized in *Tables 2–4*.

Film casting procedure

Three per cent polymer solutions in $CHCl_3$ were cast onto a flat bottom petri dish covered loosely with aluminium foil. Solvent was allowed to evaporate at ambient temperature. The bisA-NDA(80) + T(20) and bisA-T films were cast from *sym*-TCE at 70°C. For bisA-I, a mixture of $CHCl_3$ and

Table 2 Physical properties of polyarylates obtained from terephthalic acid and mediyl substituted bisphenols

Polymer	$[\eta]$ (dl g ⁻¹) ^a	d_{sp} (Å) ^b	ρ (g cm ⁻³) ^c	v_f (cm ³ cm ⁻³) ^d	δ (cal cm ⁻³) ^{1/2e}	T_g (°C) ^f
BisA-T	0.83	5.47	1.217	0.351	9.96	210
DMbisA-T	1.28	5.57	1.167	0.355	9.68	187
TMbisA-T	0.74	6.06	1.107	0.370	9.30	239
Ppha-T	0.54	5.40	1.309	0.351	10.13	—
<i>o</i> -Cp-T	0.54	5.36	1.251	0.357	9.84	—

^aOne point intrinsic viscosity using 0.1% polymer solution in phenol: *sym*-TCE (6:4 w/w).^b d_{sp} -Spacing obtained from WAXD spectra.^cDensity by flotation method at 40°C using aqueous K₂CO₃ solutions.^dFractional free volume ($v_f = 1 - V_w/V$) calculated using Van Krevelen's method¹⁶.^eHildebrand solubility parameter calculated using Small's method¹⁷.^fGlass transition temperature determined by DSC at the heating rate of 20°C min⁻¹.**Table 3** Physical properties of polyarylates obtained from methyl substituted bisphenols and I, I(50) + T(50) or NDA(80) + T(20)

Polymer	$[\eta]$ (dl g ⁻¹) ^a	d_{sp} (Å) ^b	ρ (g cm ⁻³) ^c	v_f (cm cm ⁻³) ^d	δ (cal cm ⁻³) ^{1/2e}	T_g (°C) ^f
BisA-I	0.33	5.06	1.257	0.329	10.28	180
BisA-I + T	1.50	5.15	1.221	0.349	9.99	198
BisA-NDA(80) + T(20)	0.96	— ^g	1.226	0.349	10.03	236
DMbisA-I	1.10	— ^g	1.198	0.338	9.94	162
DMbisA-I + T	0.62	5.28	1.174	0.351	9.74	161
DMbisA-NDA(80) + T(20)	1.00	5.31	1.167	0.354	9.75	194
TMbisA-I	0.50	6.07	1.123	0.361	9.43	187
TMbisA-I + T	0.56	6.06	1.118	0.364	9.39	223
TMbisA-NDA(80) + T(20)	0.96	5.83	1.123	0.367	9.41	256

^{a-f}Same as for Table 2.^g d_{sp} could not be measured from WAXD spectra.**Table 4** Various transition temperatures measured by DMA for polyarylates obtained from methyl substituted bisphenols and terephthalic acid

Polymer	Transition temperature (°C)				Method of sample preparation
	α	β	γ	δ	
BisA-T	210 ^a	31	- 87	- 126	CM
DMbisA-T	217	58	33	- 103	SC
TMbisA-T	273	103	43	- 110	CM
Ppha-T ^a	300	191	- 100, - 50	NM	SC
<i>o</i> -Cp-T ^a	314	215	38	NM	SC

^aFrom Ref. ¹¹.

CM: Compression moulding.

SC: Solution casting.

NM: Not measured.

Table 5 Permeability (P)^a coefficients and selectivities (α)^b of polyarylates obtained from terephthalic acid and methyl substituted bisphenols

	BisA-T	DMbisA-T	TMbisA-T	Ppha-T	<i>o</i> -Cp-T
P(He)	14	18	50	16.2	13.3
P(Ar)	0.84	0.38	3.30	0.84	0.44
P(N ₂)	0.37	0.23	1.43	0.41	0.15
P(O ₂)	1.88	1.12	7.30	2.15	1.04
P(CH ₄)	0.40	0.17	1.32	0.47	0.18
P(CO ₂)	8	5.8	47	11.7	5
α (He/Ar)	17	47	15	19	30
α (He/N ₂)	38	78	35	40	89
α (He/CH ₄)	35	106	38	34	74
α (Ar/N ₂)	2.3	1.7	2.3	2.0	2.9
α (O ₂ /N ₂)	5.1	4.9	5.1	5.2	6.9
α (CO ₂ /N ₂)	22	25	33	29	33
α (CO ₂ /CH ₄)	20	34	36	25	28
α (N ₂ /CH ₄)	0.9	1.4	1.1	0.9	0.8

^aIn units of 10⁻¹⁰ [cm³(STP)·cm cm⁻²·s·cm Hg] at 35°C and 1 × 10⁶N m⁻².^bRatio of pure gas permeabilities.

Table 6 Permeability (P)^a coefficients and selectivities (α)^b of polyarylates obtained from methyl substituted bisphenols and I, I(50) + T(50) or NDA(80) + T(20)

	BisA-I	BisA-I + T ^c	BisA-NDA(80) + T(20)	DMbisA-I	DMbisA-I + T	DMbisA-NDA(80) + T(20)	TMbisA-I	TMbisA-I + T	TMbisA-NDA(80) + T(20)
P(He)	8.8	16.0	12.2	8.8	13.6	12.0	37.0	47.0	41.0
P(Ar)	0.16	0.56	0.37	0.21	0.30	0.19	1.68	2.11	2.12
P(N ₂)	0.09	0.33	0.15	0.076	0.13	0.08	0.68	0.88	0.90
P(O ₂)	0.49	1.40	0.87	0.46	0.73	0.47	3.50	5.00	5.10
P(CH ₄)	—	0.40	—	0.044	0.08	—	0.53	0.72	—
P(CO ₂)	2.1	7.3	—	2.5	3.8	—	24.0	33.0	—
α (He/Ar)	55	29	33	42	45	63	22	22	19
α (He/N ₂)	98	48	81	116	105	150	54	53	46
α (He/CH ₄)	—	40	—	200	170	—	70	65	—
α (Ar/N ₂)	1.8	1.7	2.5	2.8	2.3	2.4	2.5	2.4	2.4
α (O ₂ /N ₂)	5.4	4.2	5.8	6.1	5.6	5.9	5.1	5.7	5.7
α (CO ₂ /N ₂)	23	22	—	33	29	—	35	38	—
α (CO ₂ /CH ₄)	—	18	—	57	48	—	45	46	—
α (N ₂ /CH ₄)	—	0.8	—	1.7	1.6	—	1.3	1.2	—

^aSame as for Table 5.

^bRatio of pure gas permeabilities.

^cFrom Ref. 5.

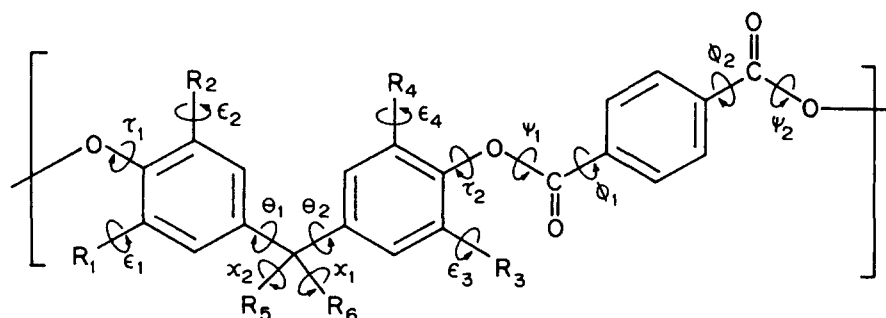


Figure 2 Various dihedral angles associated with a bisphenol + acid unit

sym-TCE was used. The formed films were peeled off after 24 h and dried in a vacuum oven at 60°C for a week in order to remove residual solvent. Complete solvent removal was verified by differential scanning calorimetry.

Permeability apparatus and procedure

The gas permeability apparatus was based on the variable-volume method; details are discussed elsewhere¹⁰. The pure gas permeability measurements were made at 35°C and at 1×10^6 N m⁻² upstream pressure while maintaining the permeate side at atmospheric pressure. Measurements were repeated (two to three times) under identical conditions. The average permeation results are summarized in *Table 5* and *Table 6*.

Molecular modelling studies

The software used and method has been described previously⁸. In this work, three polymers: bisA-T, DMbisA-T and TMbisA-T, representing unsubstituted, asymmetric and symmetric bisphenol phenyl ring substitution, respectively, were studied by molecular modelling to examine single chain conformation and bond flexibility. Polymer chain fragments consisting of eight monomer units were refined by energy minimization techniques. The various dihedral angles associated with monomer units are defined in *Figure 2*. Conformational search analyses for the energy variation as a function of the dihedral angle rotation were performed over the full rotation from 0 to 360° with regular intervals of 10° for all the dihedral angles of the central fourth and fifth monomer units to minimize chain end effects. A more detailed search with 1° increments was made near the global minima.

RESULTS AND DISCUSSION

The purpose of this work was to make a closer investigation of bisphenol substitution symmetry and acid linkage symmetry in polyarylates. The effect of asymmetric and symmetric substitution by methyl groups on the bisphenol phenyl ring has been consistently observed in several polycarbonates^{3,4}, polyarylates⁶ and polysulfones⁷. The present work investigates the reason behind the property variation by symmetry substitution using molecular modelling. First the effect of bisphenol substitution on permeation and physical properties is presented. The mechanism behind property variation as a result of bisA substitution symmetry is explained by molecular modelling studies. This is followed by a discussion of the effect of acid linkage symmetry based on results with I-, T- and NDA-based polyarylates prepared with the various bisphenols.

Bisphenol substitution symmetry

The effects of bisphenol substitution symmetry will be

examined first with the polyarylates based on terephthalic acid.

Physical properties. A comparison of *Table 2* shows that asymmetric substitution slightly increases the packing density parameters (d_{sp} and v_f) while they are increased markedly by symmetric substitution. For asymmetric substitution, it was hypothesized⁷ that the additional methyl group could be accommodated within the void space between chains, leading to decreased free volume and thus to decreased permeability than the unsubstituted case. In the case of TMbisA-T, both d_{sp} and v_f are considerably higher than the unsubstituted bisA-T polyarylate, which leads to higher gas permeability.

DMA properties for these polymers are listed in *Table 4*. Both types of bisphenol ring substitutions increased T_γ considerably. The DMA spectra of all the polyarylates based on bisA, DMbisA and TMbisA also show a δ -transition peak (which is much weaker than the γ -transition peak) in the range of -126 to -104°C (*Figure 3*).

Permeation properties. The permeation data for polyarylates based on terephthalic acid and various bisphenols are summarized in *Table 5*. The asymmetrically substituted DMbisA-T has slightly higher He permeability than the unsubstituted bisA-T. However, the permeability for other gases is markedly lower in the DMbisA case. As a result, high diffusivity dominated selectivities (He/CH₄, He/N₂) are seen in this case. CO₂-based selectivities were also found to be higher. The selectivities for other gas pairs e.g. O₂/N₂ and Ar/N₂ were similar as that of the unsubstituted bisA-T.

McHattie *et al.*⁷ reported similar trends in permeabilities and selectivities of asymmetrically substituted polysulfones (DMPSF) as found here in the case of the polyarylates. Only CO₂ and O₂ permeabilities have been reported³ for DMbisA-PC; the results show dramatically lower permeabilities for these gases in comparison to bisA-PC.

A three- to five-fold increase in permeability for different gases was observed by tetramethyl substitution in TMbisA-T, while the selectivities still remained comparable to the bisA-based polyarylates (selectivities for CO₂ were in fact higher in the TMbisA case). Except for the He related selectivities, those for other gas pairs are similar to DMbisA-T. The diffusivity related He selectivities are similar to those with bisA-T.

Muruganandam *et al.*⁴ found permeabilities three times higher and similar selectivities in TMbisA-PC as compared to bisA-PC. Symmetric substitution was also found to offer higher permeability and similar selectivity in the case of polysulfone⁷.

A comparison of permeation data for various symmetrically and asymmetrically substituted polycarbo-

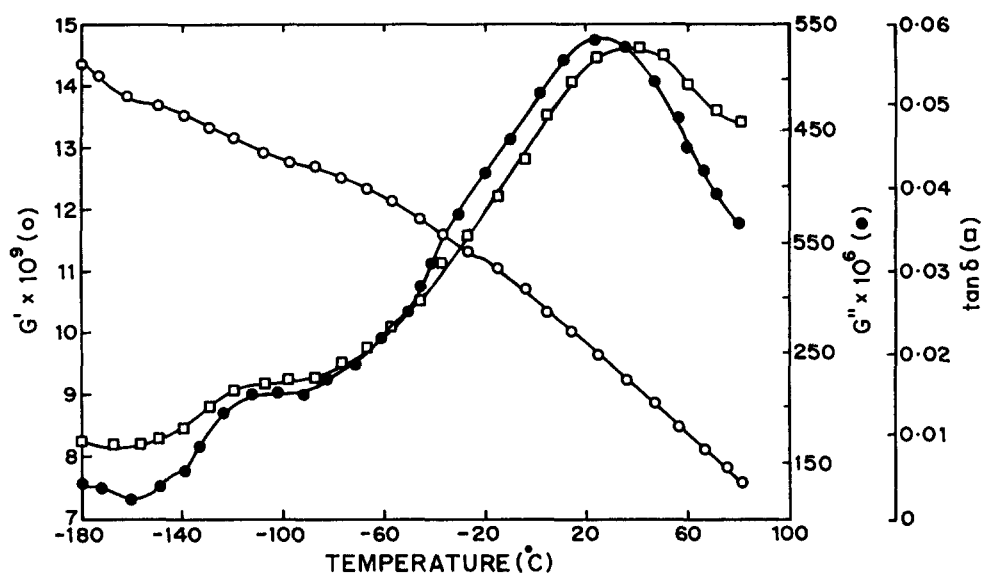


Figure 3 DMA spectra of TMbisA-T showing sub T_g transitions

nates, polysulfones and polyarylates are shown in Figure 4(a) and (b). These figures show similar substitution effects in all three types of bisphenol-based polymers. This emphasizes the need to understand the molecular basis of these structural modifications as attempted in the following sections of this paper.

Supporting evidence for effect of asymmetric bisphenol substitution: phenolphthalein-based polyarylates. The effect of the asymmetric substitution in *o*-Cp-T (a dimethyl analog of phenolphthalein) on polymer characteristics and permeation properties can be seen with reference to unsubstituted ppha-T. These property variations were observed to be similar to that of DMbisA-T *vis-à-vis* bisA-T. *o*-Cp-T has similar d_{sp} and v_f values as ppha-T. Similarly, the DMA spectra of *o*-Cp-T¹¹ shows a marked increase in γ -transition temperature and a smaller increase in T_g , when compared with the respective transition temperatures in ppha-T.

The permeabilities of He and CO₂ are reduced to a lesser extent than the permeabilities of other gases studied. The effect of asymmetrically substituted methyl groups in increasing diffusivity-based selectivity is also maintained. The He permeability of *o*-Cp-T is only 20% less than ppha-T; however, the He-based selectivities are three times higher. *o*-Cp-T also has slightly higher CO₂ selectivities than the ppha-based polymer, and the O₂/N₂ selectivity in *o*-Cp-T is significantly higher.

Molecular modelling. The molecular modelling results can be used to investigate the reason behind the property variation (e.g. packing density and chain rigidity) by bisphenol substitution symmetry. The minimum energy chain conformations of three polyarylates (bisA-T, DMbisA-T and TMbisA-T) are shown in Figure 5(a)–(d). The chain conformation characteristics observed in these polymers at their minimum energy conformations are summarized below.

Features of minimum energy chain conformations

Nonplanarity of bisphenol phenyl rings. The two phenyl rings of the same bisphenol never lie in one plane, i.e. θ_1, θ_2 can never be 0 or 180°. This is in order to avoid repulsive interactions between the two hydrogens ortho to

the bridge carbon linkage on the neighbouring phenyl rings. θ has a 180° plane of symmetry with ~2 kcal mol⁻¹ difference between global and local minima [Figure 6(a)].

Direction of chain propagation. The only sp³ hybridized (tetrahedral geometry) carbon in the monomer unit is at the bisphenol bridge position. The other atoms in the terephthalic acid-based polyarylate chain backbone are aligned such that the direction of chain propagation can change only at the bridge carbon atom.

Orientation/flexibility of bridge carbon substituents: dihedral angle χ . The bridge methyls ($\chi = \pm 60^\circ$) are always oriented outside the helical chain conformation. This type of behaviour was also noted previously for polyarylates having bridge substituent groups other than methyl⁸. The dihedral angle χ has a 120° plane of symmetry with a 7–8 kcal mol⁻¹ energy difference (ΔE) between maxima and global minima [Figure 6(b)]. The difference between global and local minima ($\Delta E'$) is 0–0.5 kcal mol⁻¹. The relative bond flexibility of 67% (as defined in our earlier work⁸) of the bridge methyls is next only to the acid phenyl ring (θ) flexibility (Table 7).

Bisphenol phenyl ring substituents: dihedral angle ϵ . This angle has plane of symmetry, relative flexibility, ΔE and $\Delta E'$ similar to that for χ . For DMbisA-T, ϵ_1 and ϵ_2 assume values of -120 and 180°. For TMbisA-T, the ϵ_3 and ϵ_4 (methyls on the second phenyl ring of bisphenol) are at 60 and 54°, respectively. However ϵ_1, ϵ_2 varied between the two sets: (0°, 60°) and (6°, 0°). The trend of this variation in ϵ_1 and ϵ_2 values could not be defined unambiguously due to the short chain fragment considered. Chains with more monomer units could not be analysed because of computer limitations.

Acid linkage (dihedral angle ϕ) and ester linkage (dihedral angle ψ). In all the polymers, the dihedral angles ψ and ϕ were 180° at the minimum energy conformational state. This is due to the electron delocalization effect¹². The angle ϕ was the most flexible dihedral angle (77% relative flexibility with $\Delta E' = 0.5$ –1 kcal mol⁻¹). The energy profile of the rotation of the dihedral angle ψ was similar to that for angle ϕ [Figure 6(b)].

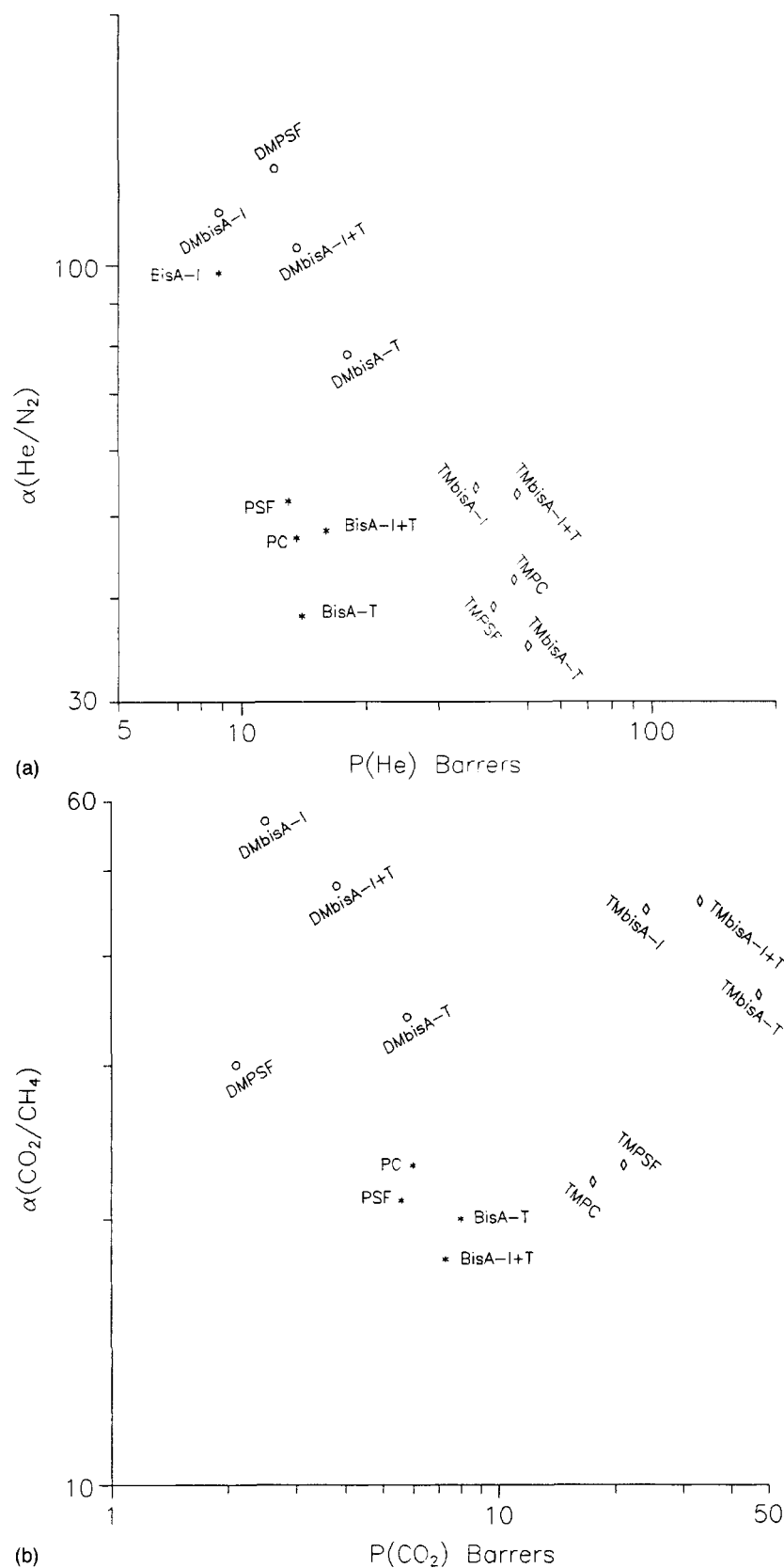


Figure 4 (a) He Permeability versus He/N₂ selectivity for unsubstituted and substituted PSF⁷, PC⁴ and PA (this work). (b) CO₂ Permeability versus CO₂/CH₄ selectivity for unsubstituted and substituted PSF⁷, PC⁴ and PA (this work)

Bisphenol dihedral angles τ and θ . These are the main dihedral angles governing chain conformation and are given in Table 8. The angle τ is sensitive to the bisphenol ring substitution. The $\Delta E'$ for this angle in bisA-T is 2–3 kcal mol⁻¹ [Figure 6(c)]. Although $\Delta E'$ increased up to 8 kcal

mol⁻¹ with methyl substitution, the relative flexibility was hardly affected.

Two chain conformations with similar minimum potential energies and differing only at the τ_2 angle were observed for TMbisA-T. The (τ_1, τ_2) dihedral angles were $(-125^\circ,$

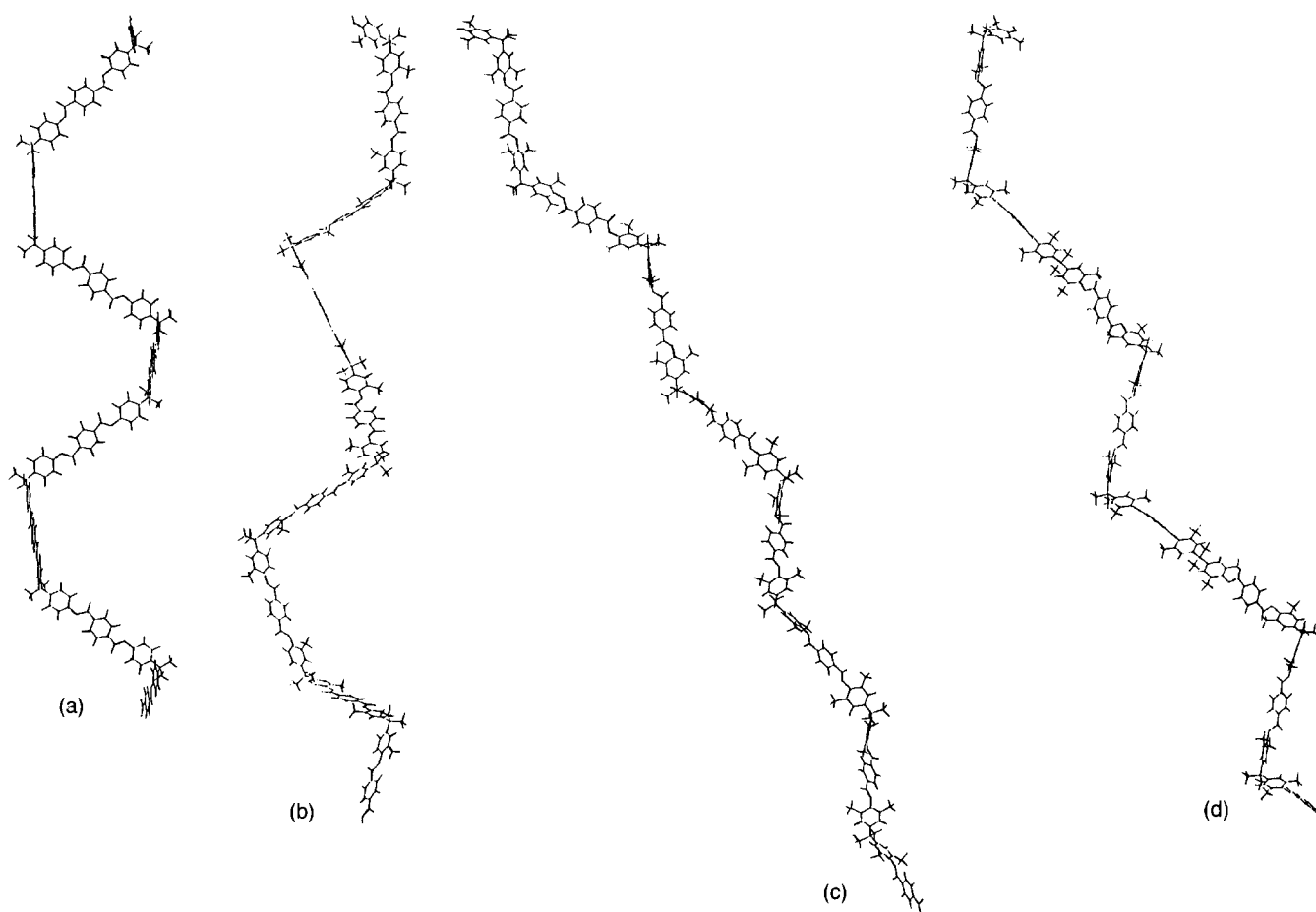


Figure 5 (a) Stick model representation of minimum energy chain conformation of bisA-T. (b) Stick model representation of minimum energy chain conformation of DMbisA-T. (c) Stick model representation of minimum energy chain conformation of TMbisA-T (I). (d) Stick model representation of minimum energy chain conformation of TMbisA-T (II)

Table 7 Average values of relative flexibility^a, entropy^a and maximum energy barrier for 360° rotation of dihedral angles in polyarylate chains

Angle	Polymer	Relative flexibility (%)	ΔE (kcal mol ⁻¹)	S (kcal mol ⁻¹ °K ⁻¹)
θ	BisA-T	46.1	3.31	159
	DMbisA-T	39.1	2.81	355
	TMbisA-T	41.0	2.94	375
τ	BisA-T	48.1	3.43	9.7
	DMbisA-T	44.4	3.19	> 10 ³
	TMbisA-I	51.3	3.68	> 10 ⁵
	TMbisA-T,II	29.3	2.10	> 10 ⁶
χ	BisA-T	67.0	4.83	10.6
	DMbisA-T	68.2	4.89	8.7
	TMbisA-T	68.0	4.87	8.8
ϵ	DMbisA-T	74.8	5.37	4.1
	TMbisA-T	72.5	5.20	5.0
ϕ	BisA-T	77.7	5.58	4.0
	DMbisA-T	78.4	5.62	4.0
	TMbisA-T	76.6	5.50	4.3

^aDefined in Ref. ⁸.

–125°) in conformation 'I' [Figure 5(c)] and (–125°, –55°) for conformation 'II' [Figure 5(d)]. These values of τ_2 are 55° displaced from the value obtained (180°) in the case of unsubstituted bisA-T.

For both the TMbisA-T conformations and also in the case of bisA-T, the dihedral angle θ_1 and θ_2 were close to 123°. For DMbisA-T, two alternate sets of dihedral angles

(θ_1, θ_2) were observed, one at (123°, 123°) and the other at (115°, 170°).

Planarity of acid phenyl and adjacent bisphenol phenyl rings. For polyarylates based on bisA and DMbisA, since ϕ and τ are both at 180°, the acid phenyl ring and the two phenyl rings (linked with the acid phenyl ring by ester

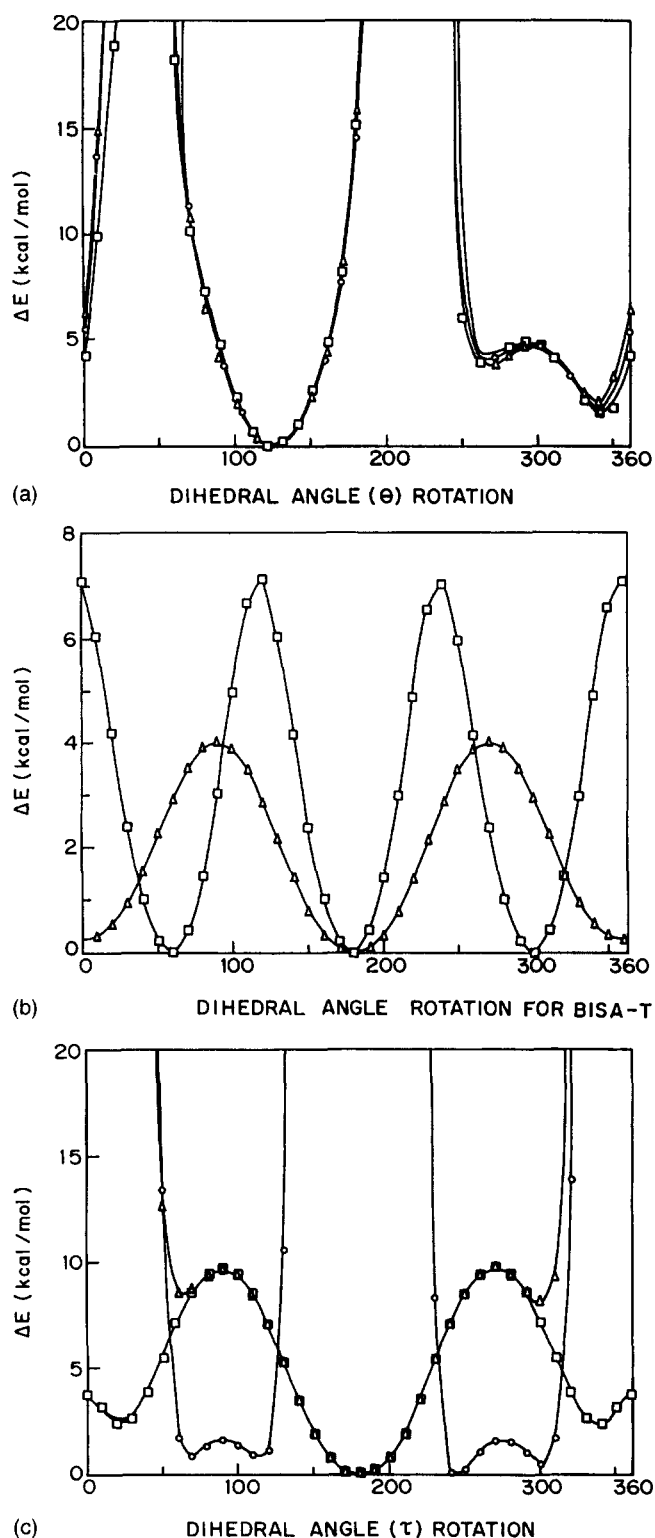


Figure 6 (a) Variation in single chain conformational energy as a function of rotation of dihedral angle θ in bisA-T (\square); DMbisA-T (Δ) and TMbisA-T (\circ). (b) Variation in single chain conformational energy as a function of rotation of dihedral angle χ (\square) and ϕ (Δ) in bisA-T. (c) Variation in single chain conformational energy as a function of rotation of dihedral angle τ in bisA-T (\square); DMbisA-T (Δ) and TMbisA-T (\circ)

linkages) of the two adjacent bisphenols preferentially lie in one plane [Figure 5(a) and (b)]. For TMbisA-based polyarylates, since τ is not at 180° , the three phenyl rings discussed above do not lie in one plane, creating a twist near the ester linkage [Figure 5(c) and (d)]. This twist on both sides of the acid phenyl ring generates an extended

conformation which is different from that of the unsubstituted and monosubstituted cases.

Physical properties: insight through conformational study

Packing density, chain rigidity and molecular mobility are the major parameters controlling gas permeation in the polymer matrix. Chain conformation can affect the packing density, while bond flexibilities obtained by conformational search analyses can be related with chain rigidity and molecular mobility. The ease of rotation of the individual moieties in the chain around their minimized (preferred) orientation will also affect the permeability through the polymer matrix.

The chain conformation is determined mainly by the two sets of dihedral angles (θ_1, θ_2) and (τ_1, τ_2). The changes in these two sets of dihedral angles alters the chain conformation, which in turn will affect the packing density of the polymer matrix. The energy variation as a function of the dihedral angle rotation for the bisphenol phenyl rings (θ and τ) and for the acid phenyl ring (ϕ) are presented in Figure 6(a)–(c). Table 7 shows that ring substitution does not change the energy environment of the relatively flexible ϕ and χ linkages.

Packing density and chain conformation. Base case: BisA-T—The preferred τ angle in the bisA-T case is 180° , which implies that the bisphenol phenyl ring and the acid phenyl ring bonded to it by an ester linkage remain in the same plane. The direction of chain propagation and the chain helix dimensions are then determined exclusively by the dihedral angles (θ_1, θ_2) associated with the bisphenol bridge carbon. These dihedral angles have a preferred orientation at 123° with an approximate symmetry of 180° . The rings can oscillate within 30 – 50° around the minimized position without encountering a significant energy barrier [< 2 kcal mol $^{-1}$, Figure 6(a)].

Asymmetric substitution: DMbisA-T—In the case of the DMbisA-based chain, the steric repulsion of the single methyl group on the bisphenol ring ensures that only one preferred orientation is available for the ester C=O group, i.e. *trans* to the ring methyl. The preferred τ value is still 180° . Although the 180° flip would no longer be possible, the bisphenol phenyl rings and the associated acid phenyl ring are still in the same plane [Figure 5(b)]. This reflects the fact that the packing density parameters of DMbisA-T are similar to bisA-T.

The preferred chain conformation is, however, different from the bisA case because of the change in the θ angles (Table 8). Instead of the single preferred pair of $\theta_1 = \theta_2 = 123^\circ$, in the DMbisA-T case it appears that the θ pair values alternate between this set and another set with $\theta_2 = 170^\circ$ (relatively flexible) and $\theta_1 = 115^\circ$ (less flexible). The result is a more extended chain (helical loop with smaller diameter) and a possibly alternating sequence of θ dihedral angles.

Symmetric substitution: TMbisA-T—In the case of either TMbisA-T conformation, the symmetrically positioned methyl groups prevent 180° τ orientation. While electron delocalization¹² would tend to force the τ dihedral angle to 180° (planar configuration), steric repulsion between hydrogen atoms of the ring methyls and the carbonyl oxygen would tend to force this angle to 90° (perpendicularly aligned to the phenyl rings where repulsive interactions would be minimum). The preferred τ values of -55 or -125° appears to be a compromise between these two forces. Thus the planarity of the bisphenol phenyl rings with the acid phenyl ring is lost and a twist near the ester linkage

Table 8 Dihedral angles governing the minimum energy chain conformation for bisA-T, DMbisA-T and TMbisA-T

Polymer	θ_1	θ_2	τ_1	τ_2
BisA-T	123	123	180	180
DMbisA-T	123/115	123/170	180	180
TMbisA-T (I)	123	123	- 125	- 125
TMbisA-T (II)	123	123	- 125	- 50

takes place before the propagating chain direction changes at the bisphenol bridge carbon. Additionally these TMbisA phenyl rings are only able to oscillate in a narrow range. Such conformations may not allow close chain packing. Thus TMbisA has significantly higher v_f and d_{sp} than either bisA-T or DMbisA-T, where the planarity of the three phenyl rings is maintained.

Chain rigidity and relative flexibility. The energy barrier (ΔE), entropy (S) and relative flexibility for the bond rotation of individual moieties would determine the chain rigidity.

The γ -transition in these polyarylates has been assigned mainly to the bisphenol phenyl ring motions¹¹. In the case of the bisphenol ring substituted polyarylates, it would be expected that T_γ would increase from -80° in the bisA case. This is seen for both the DMbisA and TMbisA polymers where T_γ now occurs at 30 – 50° .

In case of bisA-T, the τ rotational barrier is relatively low, hence it would be relatively easier for the C=O group to flip between two positions, 180° displaced from each other. When the bisphenol-A phenyl ring is asymmetrically substituted, a large increase (10^3 kcal mol⁻¹) in the energy barrier for this flip takes place. The high energy barrier is caused by the repulsive interactions of hydrogens of the ortho methyl group with the carbonyl oxygen. This explains the high γ -transition temperature observed in the DMA spectra of DMbisA-based polyarylate. The slightly higher γ -transition temperature in TMbisA polyarylates can be explained on similar grounds.

Next to τ , θ is the most restricted dihedral angle. If the γ -transition can thus be attributed to τ rotation of the bisphenol phenyl ring; the δ -transition may be attributed to rotation of the θ dihedral angle. This hypothesis needs to be confirmed by further DMA investigations.

Permeation properties: insight through molecular modelling

Molecular modelling shows that in DMbisA-T, the planarity around the acid phenyl ring is retained (same τ); however, the chain conformation is extended due to changes in θ . The retention of phenyl ring planarity may correlate with the similar packing densities in DMbisA-T and bisA-T, while the extended chain conformation may correlate with the ability of the polymer matrix to discriminate between permeating species on a steric basis. These factors may be responsible for retention of He permeability while increasing selectivity.

In the TMbisA-T case, the chain conformation due to the θ dihedral angles is similar to the bisA case; however, the planarity around the bisphenol phenyl ring is lost and chain packing density is decreased. These factors may be responsible for retention of selectivities while increasing permeability.

ACID LINKAGE SYMMETRY

In the previous section, the effects of bisphenol substitution symmetry in polyarylates with the symmetrically (para) linked acid are discussed. In this section, we also examine polyarylates based on the asymmetrically linked acid: isophthalic acid (I) and a larger rigid acid: 2,6-naphthalene dicarboxylic acid (NDA). The NDA also has symmetrical placement of acid linkages similar to terephthalic acid.

A comparison of the polyarylates based on bisA, DMbisA and TMbisA with terephthalic acid (symmetric or para linkage), an equimolar mixture of iso- and terephthalic acid, and isophthalic acid (asymmetric or meta linkage) allows us to examine the effect of acid symmetry (Tables 2, 3, 5 and 6).

Physical properties

For any given acid, the variation in the physical properties of the resulting polyarylates with bisA, DMbisA and TMbisA are similar to that of their terephthalic acid-based polymers. The polymer rigidity, as evidenced by its T_g , increases in the order $I < I + T < T$ for any given bisphenol. The polyarylate packing densities and solubility parameters generally increase in the order $T < I + T < I$ for all these bisphenols (Tables 2 and 3). The chain conformation of bisA-T is of the crank-shaft type, for which three monomers are required to form a helical loop. Previously it was shown that bisA-I has a regular helical conformation in which one loop is formed by just one monomer unit¹³. While the direction of chain propagation in the T-based polyarylates can change only at the bisphenol bridge carbon, the chain propagation direction for I-based polyarylates can also change at the acid group. Preliminary packing analyses using molecular modelling demonstrated better packing of bisA-I than bisA-T in qualitative agreement with the experimental d-spacing.

Permeation properties

For polyarylates of all bisphenols based on either I, I + T or T acid, gas permeability increased in the expected order: $I < I + T < T$. The selectivity of various gas pairs followed the reverse order.

As mentioned earlier, the terephthalic-based polyarylates have lower He selectivities than the polyarylates with other acids. The He selectivities in DMbisA-T are considerably higher than those in bisA-T with similar He permeability, while TMbisA-T has about a three times higher He permeability with similar selectivity.

By contrast, in the case of the isophthalic acid-based polyarylates, it is seen that the bisA polyarylate itself has high diffusivity-based selectivity ($He/N_2 = 98$). Neither permeability nor selectivities for He are affected when DMbisA is used in place of bisA, although there is an increase in the CO_2/N_2 selectivity of about 50%. When the permeabilities of DMbisA-based polymers were compared with the corresponding polymers based on bisA, it was

observed that among the isomers, DMbisA-T showed a greater decrease in permeability in comparison to bisA-T. Comparatively, a smaller decrease in permeability was shown by DMbisA-I in comparison to bisA-I. The He permeability of TMbisA-I is roughly four times higher than that of bisA-I with reduced selectivity for He. The CO₂/N₂ selectivity of TMbisA-I is similar to that of DMbisA-I.

The permeation properties of bisA-I and bisA-T are reported by Pessan and Koros¹⁴ while that of DMbisA-I and TMbisA-I are reported by Pixton and Paul⁶. Our permeability values for bisA-T, DMbisA-I and TMbisA-I generally agree with the reported data. However, for bisA-I, we find lower permeability than the reported values. Pessan and Koros¹⁴ used special film casting procedures in order to avoid crystallinity. In our study, we have not taken such special care; however, the absence of crystallinity in our bisA-I samples was verified by both WAXD and DSC.

Supporting evidence for effect of symmetric acid linkage: NDA-based polyarylates

80:20 NDA:T-based polyarylates have similar packing density as that of terephthalic acid-based polyarylates. The additional increased rigidity due to the naphthalene ring incorporation results in the highest He/N₂ selectivities. The trends in the permeabilities and selectivities with methyl substitution of the bisphenol phenyl rings are similar to those with the polyarylates based on bisA, DMbisA and TMbisA with either terephthalic acid alone or the 50:50 I:T acids mixture. This can be seen by comparing data for NDA-based polyarylates in Table 6 with those for other polyarylates.

POSSIBLE POLYARYLATE SYNTHESIS STRATEGIES WITH REFERENCE TO BISPHENOL/DIACID SUBSTITUTION SYMMETRY

The higher permeability and retention of selectivity of the TMbisA-based polymers in comparison to bisA-based polymers can be rationalized by an empirical rule¹⁵ as being the consequence of a simultaneous increase in polymer chain rigidity accompanied by reduced packing density. It has been suggested⁷ that in the case of the asymmetric substitution, the bulk of the methyl group fills the void space between chains, resulting in less free volume than the unsubstituted case. Because of this, these polymers show low permeability, but they are more selective.

On a molecular level, it is seen that the preferred chain conformation with the asymmetrically substituted DMbisA-based polymer retains the planarity of phenyl rings, but is more extended at the bridge carbon position. The phenyl ring planarity cannot be maintained in the TMbisA case. The use of an asymmetrically linked acid (I) leads to a shorter chain helical loop as compared to the para linked acid (T).

Experimentally, it is seen that DMbisA-based polymers have similar packing densities and lower phenyl ring rotational mobility than the bisA polymers. The permeabilities of the smaller gas (He) are comparable while those for gases with larger molecular sizes are considerably lower. These leads to significantly higher diffusivity controlled selectivities (e.g. He/CH₄, He/N₂ or He/Ar) while those for other gas pairs (O₂/N₂, CO₂/N₂) are also generally improved.

TMbisA-based polymers have significantly lower packing density and are also more rigid than the bisA analogues. Permeabilities are significantly increased for all gases while He related selectivities are either similar or marginally

decreased. The selectivities for CO₂ with respect to CH₄ or N₂ are improved.

The above-mentioned trends hold in polyarylates, poly-sulfones and polycarbonates [see Figure 4(a) and (b)]. The effect of the asymmetric substitution in increasing He related selectivities also appears to hold in phenolphthalein-based polyarylates as well as in bisA-based polymers. The trends are also independent of the acid used for synthesizing the polyarylate. However, the effect of the asymmetric bisphenol substitution in increasing selectivity is most marked when in conjugation with symmetrically linked acids. The effect of the symmetric bisphenol substitution in increasing permeability is most marked in conjugation with the asymmetrically linked acid. This gives the opportunity for rational design of the polyarylate by combining an asymmetrically substituted diol (high selectivity) or a symmetrically substituted diol (high permeability) with the appropriately linked acid. Polyarylates based on the asymmetrically (meta) linked isophthalic acid have higher selectivity and lower permeability than those based on the symmetrically (para) linked terephthalic acid. The highest permeability is obtained when the symmetrically linked acid is combined with the symmetrically substituted bisphenol. The highest selectivity is obtained when the asymmetrically linked acid is combined with the asymmetrically substituted bisphenol. Thus by combining the symmetrically substituted TMbisA diol with an asymmetrically linked diacid such as isophthalic acid, both He permeability and selectivity can be simultaneously enhanced. Similarly combining the asymmetrically substituted DMbisA diol with a diacid such as terephthalic acid, both high He selectivity and permeability can be obtained. Incorporation of the naphthalene acid also gives rise to higher selectivities for small gases.

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