Gas Transport Properties of a Series of High T_g Polynorbornenes with Aliphatic Pendant Groups

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ABSTRACT: A study of gas transport properties of novel polynorbornenes with increasing length of an aliphatic pendant group R (CH_3—, $CH_3(CH_2)_3$—, $CH_3(CH_2)_5$—, $CH_3(CH_2)_9$—) has been performed. These polymers were synthesized using novel organometallic complex catalysts via an addition polymerization route. This reaction route maintained the bridged norbornene ring structure in the final polymer backbone. Gas permeability and glass transition temperature were found to be higher than those for polynorbornenes prepared by ring-opening metathesis and reported in the literature. It was shown that for noncondensable gases such as H_2 and He the selectivity over N_2 decreased when the length of the pendant group increased, but remained relatively stable for the more condensable gases (O_2 and CO_2). The permeability coefficient is correlated well to the inverse of the fractional free volume of the polymers. The more condensable gases showed a deviation from this correlation for the longest pendant group, probably due to an increase of the solubility effect. This polymer series demonstrated a simultaneous increase in permeability and selectivity, uncommon for polymers. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 797–803, 1998
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INTRODUCTION

Polynorbornenes have been synthesized for their excellent properties for dielectric applications, and also for their significant cost advantage in comparison with materials currently used as interlevel dielectrics in microelectronics.[1] Their transport properties are important not only for this application, but also for other potential uses in packaging[2] and gas separation.[3] The most familiar polynorbornene[4–9] (Fig. 1) is prepared by ring-opening metathesis polymerization (ROMP) and has a varying content of *cis* and *trans* units, depending on the polymerization catalyst used. The ROMP polynorbornenes have been the subject of a number of investigations; some of which are summarized below. In contrast, the polynorbornenes evaluated here have been synthesized via a novel addition polymerization, which maintains the norbornene ring structure. For simplicity, we will refer to these as addition polynorbornenes (APNBs). The molecular architecture of the APNBs, shown in Figure 2, is fundamentally different than the ROMP polymers shown in Figure 1. The impact of this difference on the physical and transport properties is the subject of this study.

Yampol'skii et al.[6] studied the transport properties of ROMP polynorbornenes with different stereoregular structures controlled by the synthesis. They showed that the polynorbornene with predominantly *cis* units in the backbone chain shows higher gas permeabilities than those with predominantly trans units. They also determined the free volume of their polymers by the positron

Figure 1. Repeat unit of ROMP polynorbornene polymerized by ring-opening metathesis.

annihilation method. Steinhäusler and Koros[7] have also investigated the influence of stereochemistry and tacticity of ROMP polynorbornenes on gas separation properties, and reported findings similar to Yampol'skii.

Bondar et al.[8] studied permeation and sorption in polynorbornenes with varying substituents. They reported that the introduction of a $Si(CH_3)_3$ group to the backbone increased the glass transition temperature and the permeability of gases through the polymer. They concluded that if the size of the silicon-containing side group is too large, the permeability and the glass transition decrease (see Table IV). Yampol'skii et al.[9] observed increased gas permeability, gas sorption, and elevated glass transition temperatures in polynorbornenes with fluorine-containing side groups.

In the research reported here, we have investigated a class of polynorbornenes, which retain the norbornene ring in the repeat unit, as shown in Figure 2. This structure is substantially more rigid than the polynorbornenes prepared by ring-opening metathesis polymerization as previously discussed.[4–9] Thus, we anticipate that our materials will have enhanced glass transition temperatures and potentially improved separation selectivities. We have investigated the effect of the size of aliphatic pendant groups on transport properties.

EXPERIMENTAL

Materials

The repeat unit for the polynorbornene materials evaluated here is shown in Figure 2, where R represents different pendant groups. The polynorbornenes were supplied by the B. F. Goodrich corporation. They were produced via addition polymerization using an organometallic complex as catalyst.[10–12] APNBs with four different pendant groups have been evaluated here. The pendant groups are methyl, butyl, hexyl, and decyl. The

elongation-to-break of the unsubstituted APNB was insufficient to allow for formation of the film samples needed for permeation evaluation.

Polymer samples were cast from chloroform (Aldrich, 99.9% purity, used as received). Permeation samples were prepared by adhering aluminum foil masks to the polymer with an epoxy adhesive (Duro Master Mend).[13] All gases (minimum purity 99.9%) were obtained from Air Products and used as received.

Preparation

The films were cast from the chloroform solution containing approximately 3.6 wt % of polymer. The solution was filtered through a 0.45-μm Teflon filter and cast directly into a stainless steel ring on a leveled mirror. A second glass plate was placed across the top of the casting ring to slow the evaporation of the solvent. The evaporation was performed in a glove bag in a solvent-enriched environment. After 24 h, the films were removed from the plates by immersion in water. The films were further dried under vacuum at 100°C to a constant weight. In the initial 7 h of vacuum drying, a weight loss of 2% was measured. Continued drying to a total of 24 h resulted in no further change in weight. The vacuum system was equipped with a trap to prevent oil vapor back diffusion.

Thickness and Area Measurement

After drying, the film thicknesses were measured. A known area of the film was weighed, and using the measured density (see below), the film thickness was calculated. The accuracy of this thickness measurement was determined by repeated measurements and was estimated to be within 2% of the reported value. The thickness of our films
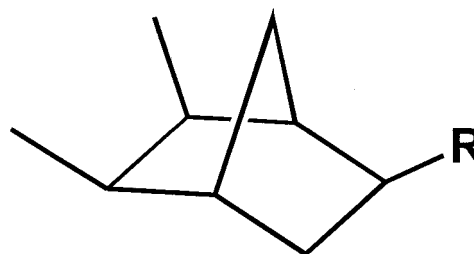
Figure 2. Repeat unit of addition polynorbornene (APNB) polymerized by using an organometallic complex as the catalyst (prepared by B. F. Goodrich, R see Table I).

ranged from 6–12 μm. Thickness measurements with a mechanical gauge (resolution 1 μm) were in good agreement with the method described above.

The permeation area was determined by successive magnified photocopies of the masked permeation area taken after the end of the experiments. The image of the permeation area was then determined gravimetrically. The average area determined by the above procedure ranged from 1 to 13 cm² with an error of about 1%.

Permeation Measurement

The permeability was studied by single-gas permeation using a constant-volume/variable-pressure apparatus. The permeation cell was maintained at 35°C ± 0.1°C. The feed pressure was 10 ± 0.05 atm; on the permeate side of the film, the gas pressure was less than 10 Torr and considered negligible. The leak rate into the vacuum system introduced an error for the permeability measurement of less than 0.01% for the slowest gas. These techniques have been described in greater detail, for example, by Koros.[14]

Density Measurement

The density measurements were performed at 23 ± 0.1°C with a density gradient column, using iso-propanol/water–calcium nitrate solutions. Samples were cut from the same samples used in the permeability measurement. Solvent uptake during the density measurement was less than 0.2 wt %.

RESULTS AND DISCUSSION

Physical Properties

A polymer's glass transition temperature, T_g, is related, among other parameters, to the rigidity of the macromolecule. The thermal properties of these polynorbornenes were measured using dynamic mechanical thermal analysis at the B. F. Goodrich Corporation.[15] The results are summarized in the second column of Table I. The increasing length of the flexible pendant group results in a decrease in the glass transition temperature and modulus of these polymers. The polynorbornene with the methyl side group has the highest glass transition temperature of this group (above 380°C). The polynorbornene with the decyl side group has the lowest glass transition temperature

(about 150°C). For comparison, the glass transition temperatures of the ROMP polynorbornenes are presented in Table IV. The ROMP polymers have consistently lower T_gs. Thus, we can conclude that the APNB polynorbornene backbone is less flexible than the ROMP polymers.

Fractional Free Volume Determination

The relation between the free volume and the coefficient of viscosity, η, was introduced by Doolittle in 1951[16] as:

$$\eta = A \exp[B/(v_o/v_f)] \tag{1}$$

where A and B are constants. The fractional free volume (FFV) is defined as v_f/v_o:

$$\text{FFV} = (v - v_o)/v_o = v_f/v_o \tag{2}$$

where v is the total specific volume of the polymer; v_o is the so-called "occupied volume," which cannot assist in penetrant transport; and v_f is the specific free volume of the polymer. Using the Stokes–Einstein relation with a_o as the diameter of a sphere having the volume of the molecule, the diffusion coefficient, D, can be written as:

$$D = (kT/\pi a_o)/\eta \tag{3}$$

where T is the temperature, and k is Boltzmann's constant.

Cohen and Turnbull[17] derived the relation between the diffusion coefficient and the fractional free volume as:

$$D = D_o \exp[-\gamma v^*/v_f] \tag{4}$$

where v^* is the critical volume just large enough to permit displacement of molecules. The permeability coefficient can be written as the product of the diffusion coefficient and the sorption coefficient, in the absence of significant swelling:

$$P = DS \tag{5}$$

The pendant groups of our polynorbornenes can be written as $CH_3(CH_2)_x$—. As one evaluates the polymer series reported here, only the length of the aliphatic side chain changes (represented by x). If it is assumed that the solubility coefficient does not change significantly, the permeation co-

Table I. Physical Properties of APNB Polynorbornenes: Van der Waal's Volume and Free Volume Estimated from Group Contribution Methods

Polynorbornene Pendant Group (R)	$T_g{}^a$ (°C)	Young's Modulus[a] (GPa)	ρ^b (g/cm^3)	v_w (cm^3/g)	v_f (cm^3/g)	FFV
1. CH_3—	Exceeds 380	1.4	0.986	0.6302	0.1949	0.1922
2. $CH_3(CH_2)_3$—	Exceeds 350	0.9	0.970	0.6579	0.1756	0.1704
3. $CH_3(CH_2)_5$—	280	0.6	0.965	0.6691	0.1664	0.1606
4. $CH_3(CH_2)_9$—	150	0.2	0.946	0.6835	0.1685	0.1594

[a] See reference 15.
[b] at 23°C.

efficient, P, and the ideal selectivity, $\alpha^*_{A/B}$, can be described as follows:

$$P = P_o \exp[-\gamma v^*/v_f] \qquad (6)$$

$$\alpha^*_{A/B} = P_A/P_B \qquad (7)$$

where P_A and P_B are the permeation coefficients for two different gases A and B. P_o and γ are constants.

Table I presents the volumetric data of polynorbornenes. The free volume was calculated using the Bondi[18] method. The specific volume, v_{sp}, is defined as $1/\rho$, where ρ, the density, was experimentally measured. The van der Waal's volume, v_w, was estimated by using van Krevelen's[19] data. Thus, the free volume is given by

$$v_f = v_{sp} - 1.3v_w \qquad (8)$$

and the fractional free volume can be calculated as

$$\text{FFV} = v_f/v_{sp} \qquad (9)$$

The greatest challenge for this calculation is the van der Waal's volume of the norbornene ring structure. We approximated this volume by building up the ring in a step-wise fashion from known components. Although this may introduce error in the exact fractional free volume values calculated, errors in this calculation should not seriously influence the comparison between the different pendant groups, because the same ring is present in all polymers investigated here. The calculated fractional free volumes are presented in Table I.

Permeation

Table II presents the permeability coefficients for different gases at 35°C and 10 atm. The permeability coefficient decreased with increasing size of the pendant group except for the last value, which showed an increase in the permeability coefficient. Figure 3 presents the H_2 permeability coefficient vs. the inverse fractional free volume for these polymers (numbered 1–4 in the figure) and selected data from the literature. The polynorbornenes evaluated here exhibit good correlation between the experimental permeabilities and the inverse of fractional free volume. Similar relationships also existed for the other gases examined. The good correlation observed for these polymers could be explained by the fact that our pendant groups present the same structure, and therefore, the solubility of gases in these materials is approximately constant across the entire family.

The overall correlation between hydrogen permeability and the inverse of fractional free volume for our APNBs evaluated and the ROMP polymers from the literature shows some scatter. The inability of this correlation to account for differences in the polymer backbone has been previously observed.[20,21] Indeed, this behavior provides further evidence that differences in polymerization routes, which result in dissimilar polymer backbones, are important in determining the properties of the polymers.

Selectivity

Table III presents the ideal selectivity for different gases over nitrogen and methane. The selectivity decreased with increasing pendant group length for all gases. The percentage change was the largest for the noncondensable gases such as

Table II. Single Gas Permeability Coefficients at 35°C and 10 atm for APNB Polynorbornenes

Polynorbornene Pendant Group (R)	Barrer[a]					
	N_2	H_2	O_2	CO_2	CH_4	He
1. CH_3—	24.1	502.1	89.2	396.3	30.3	309.4
2. $CH_3(CH_2)_3$—	11.2	110.7	33.3	141.9	28.4	66.7
3. $CH_3(CH_2)_5$—	6.9	57.2	19.8	83.8	18.7	36.8
4. $CH_3(CH_2)_9$—	8.7	62.4	25.3	111.1	28.1	38.9

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

He and H_2, and less pronounced for more condensable gases such as CO_2 and O_2. The CH_4/N_2 selectivity was the only gas pair that showed an increase in selectivity with increasing side group length.
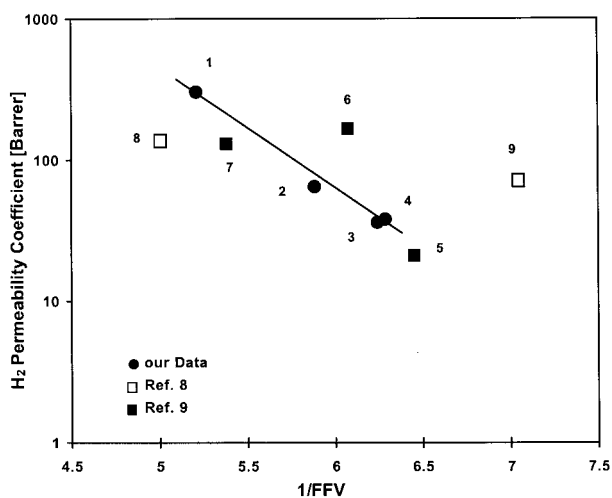
Comparison to Other Polynorbornenes

Table IV presents permeability coefficient data measured by other researchers. The first three lines of the table give Yampol'skii's[9] data for fluorinated polynorbornenes. Both the permeability of our polynorbornene with the CH_3 pendant group and its T_g are higher than for the polymers present in this table. For the rest of our polymers, some permeability coefficients are lower, but the high T_g is maintained. The second part of this table presents Bondar's data.[8] Although glass transition temperatures of polynorbornenes with

Figure 3. Correlation between inverse fractional free volume of APNB polynorbornenes and the permeability coefficient for H_2. Comparison with literature data (Table I and Table IV). (1 Barrer = 10^{-10} cm^3 (STP) cm/ cm^2 s cmHg).

organosilicon substituents are consistently lower than those for our APNBs in Table I, no clear trend in the permeability coefficients is apparent.

Direct comparison of ROMP and APNB polynorbornenes is complicated by the slight variations in the side groups of the materials studied. For the APNB series evaluated, both permeability and selectivity decrease as the length of the aliphatic side group is increased. Although extrapolation of this trend to predict the performance of other materials should be viewed with caution, we hypothesize that the properties of the unsubstituted APNB would be similar to those of the APNB with the methyl side group. Indeed, the glass transition temperature of the unsubstituted material[15] is above 400°C, as would be expected from extrapolation of data for the substituted materials.

Comparing the properties of the unsubstituted ROMP polynorbornene (polymer 5 in Table IV) with the methyl-substituted APNB (polymer 1 in Tables I–III), one can gain insight into the importance of the rigidity of the polymer backbone in these polymers. The permeability of H_2 through these polymers is about 500 Barrer for the APNB materials, but only 21 Barrer for the ROMP polymer. Hydrogen/nitrogen selectivities are 20.8 and 14, and the T_gs are above 380 and 31°C, respectively. Thus, the APNB has higher permeabilities, higher selectivities, and a higher glass transition temperature than the corresponding ROMP material. One might expect, therefore, that an APNB material with a fluorinated side group (such as the ROMP polymer 6) might have even more attractive properties.

Comparison to Gas Transport in Other Polymers

The polymers studied here show increasing permeabilities with increasing selectivities, as can be seen in the H_2/N_2 tradeoff curve in Figure 4.

Table III.   Ideal Selectivity Coefficients for APNB Polynorbornenes (Calculated from Single Gas Permeability Coefficients)

Polynorbornene Pendant Group (R)	H_2/N_2	O_2/N_2	He/N_2	CO_2/N_2	CH_4/N_2	CO_2/CH_4	H_2/CH_4
1. CH_3—	20.8	3.7	12.8	16.4	1.2	13.0	16.5
2. $CH_3(CH_2)_3$—	9.9	3.0	5.9	12.6	2.5	4.9	3.9
3. $CH_3(CH_2)_5$—	8.3	2.9	5.3	12.2	2.7	4.4	3.0
4. $CH_3(CH_2)_9$—	7.2	2.9	4.5	12.8	3.2	3.9	2.2

Robeson's upper bound[22] is also shown for reference. The behavior of this polymer family is somewhat unusual, because for many polymers permeability decreases with increasing selectivity. According to previous work by Hoehn,[23] the behavior of our polymers can be rationalized by considering qualitatively the properties of the polymer chains and the free volume in the polymer. In the absence of significant sorption effects, the simultaneous selectivity increase with increased permeability can be explained as follows:

The increasing selectivity with decreasing length of the flexible side chain is due to increasing influence of the rigidity of the polymer backbone. Rotational mobility decreases with increasing influence of the stiff backbone on the polymer properties. This, according to the ideas presented by Hoehn[17] and Koros,[24] will increase selectivity.

The flexibility of our polymer molecules increases with the side-chain length ($CH_3(CH_2)_x$—). This is evident from the decrease of T_g with increasing side-chain length. At the same time, the side group is linear and packs well. Improved packing of the polymer chains is apparent from the decrease of fractional free volume with increasing side-chain length. This is strongly related to a permeability loss.

The transport data for this family of polymers with a rather stiff backbone and a flexible side chain show how the properties of polymers can be tailored by molecular-level changes. It is even possible to reverse the tradeoff between selectivity and permeability that is often found.

CONCLUSIONS

Maintaining the norbornene ring structure in the polymer backbone is important to obtain high glass transition temperatures and gas permeabilities. This study of the transport properties of polynorbornenes with aliphatic pendant groups further shows that an increase in pendant group chain length is responsible for the simultaneous decrease in fractional free volume, glass transition temperature, permeation coefficients, and

**Table IV.**   Properties of ROMP Polynorbornenes

Polynorbornene	ρ (g/cm^3)	FFV	T_g (°C)	Barrer[a]					
				N_2	H_2	O_2	CO_2	CH_4	C_2H_6
No side chain									
5. PNB[b]	0.98	0.156	31	1.5	21	2.8	15.4	2.5	1.4
Fluorine-containing side chains									
6. PFMNB[b]	1.586	0.165	169	17	166	50	200	13	6.6
7. POFPNB[b]	1.626	0.187	77	17	130	55	200	18	14
Silicone-containing side chains									
8. PTMSNB[c]	0.92	0.200	113	7.2	140	30	89	17	7
9. PDSNB[c]	0.93	0.142[d]	24	3.7	73	16	67	8.5	10

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.
[b] Measurements performed at 22 ± 3°C and 50–500 Torr (ref 9.).
[c] Measurement performed at 22 ± 1°C, 10–200 mmHg, and the low-pressure side was about 10^{-3} mmHg (ref 8.).
[d] Calculated by authors using Bondi method.
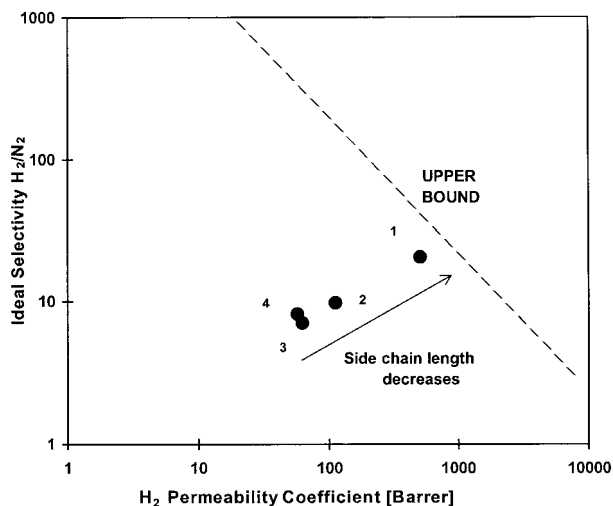
Figure 4. Relative position of our polynorbornenes in comparison with Robeson's upper bound.[22] Permeability and selectivity increase simultaneously with decreasing side group length. (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg).

permselectivity. Interestingly, the APNB polymer family investigated shows simultaneous increases in selectivity and permeability as the pendant chain length is decreased. This behavior may prove important for future attempts to move beyond the performance of current polymers.

REFERENCES AND NOTES

1. N. R. Grove, P. A. Kohl, S. A. Bidstrup–Allen, R. A. Shick, B. L. Goodall, and S. Jayaraman, Proceedings of the International Conference on Multichip Modules, IMAPS and IEEE, 224–227, April 7, 1997.
2. M. Salame, TAPPI Proceedings—Polymers, Laminations and Coatings Conference, TAPPI Press, 1986, p. 363.
3. V. T. Stannett, W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, *Adv. Polym. Sci.,* **32,** 69 (1979).
4. D. R. Paul and Y. P. Yampol'Skii, *Polymeric Gas Separation Membranes,* CRC Press, Boca Raton, FL, 1994.
5. Y. Kawakami, H. Toda, M. Higashino, and Y. Yamashita, *Polym. J.,* **4,** 285 (1988).
6. Y. P. Yampol'skii, E. S. Finkel'shtein, K. L. Makovetskii, I. Y. Ostrovskaya, E. B. Portnykh, M. L. Gringol'ts, Y. G. Ishunima, I. B. Kevdina, and V. P. Shantarovich, *Polym. Sci.,* **38,** 1480 (1996).
7. T. Steinhäusler and W. J. Koros, *J. Polym. Sci., Polym. Phys.,* **35,** 91 (1997).
8. V. I. Bondar, Y. M. Kukharskii, Y. P. Yampol'skii, E. S. Finkel'shtein, and K. L. Makovetskii, *J. Polym. Sci., Polym. Phys.,* **31,** 1273 (1993).
9. Y. P. Yampol'skii, N. B. Bespalova, E. S. Finkel'shtein, V. I. Bondar, and A. V. Popov, *Macromolecules,* **27,** 2872 (1994).
10. B. L. Goodall, G. M. Benedikt, L. H. McIntosh, III, D. A. Barnes, and D. A. Medina, U.S. Pat. 5,468,819 (1995).
11. B. L. Goodall, G. M. Benedikt, L. H. McIntosh, III, D. A. Barnes, and L. F. Rhodes, U.S. Pat. 5,569,730 (1996).
12. B. L. Goodall, G. M. Benedikt, L. H. McIntosh, III, D. A. Barnes, and L. F. Rhodes, U.S. Pat. 5,571,881 (1996).
13. P. H. Pfromm and W. J. Koros, *Polymer,* **36,** 2379 (1995).
14. W. J. Koros, Ph.D. Dissertation, University of Texas at Austin (1977).
15. R. A. Shick, Personal Communication, B. F. Goodrich Corporation (1997).
16. A. K. Doolittle, *J. Appl. Physiol.,* **22,** 1031 (1951).
17. M. H. Cohen and D. J. Turnbull, *J. Chem. Phys.,* **31,** 1164 (1959).
18. A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses,* Wiley, New York, 1968.
19. D. W. van Krevelen, *Properties of Polymers,* Elsevier, New York, 1990.
20. Y. Maeda and D. R. Paul, *J. Polym. Sci., Polym. Phys.,* **25,** 1005 (1987).
21. D. H. Weinkauf and D. R. Paul, *J. Polym. Sci., Polym. Phys.,* **30,** 837 (1992).
22. L. M. Robeson, *J. Membr. Sci.,* **62,** 165 (1991).
23. H. H. Hoehn, U.S. Pat. 3,822,202 (1974).
24. W. J. Koros, M. R. Coleman, and D. R. B. Walker, *Annu. Rev. Mater. Sci.,* **22,** 47 (1992).