The IR spectra of PI films are also presented in Figure 2. The same absorption bands are observed in the spectra of an original PI film and of a laser-irradiated PI film. The main absorption bands[18-20] associated with C=O (1705 cm^{-1}), C-N (1362 cm^{-1}), C-O (1076 cm^{-1}), and aromatic rings (733 and 1516 cm^{-1}) appear in the spectra. The penetration depth of 248-nm laser light in a PI surface is limited to about 200 nm due to strong absorption of PI.[21,22] Also, the penetration depth of the IR monitoring beam in a PI film seems to be of the same order as that in a PET film.

An example of a PI difference spectrum obtained by subtraction method mentioned above with a scale factor of 0.82 is shown in Figure 2c. In the region of 900-4000 cm^{-1}, the absorption bands similar to those of PET are seen under the base line due to using a large scale factor, and there is no characteristic band of the modified surface. However, in the region of 450-900 cm^{-1}, several absorption bands are seen above the base line and can be identified as characteristic bands of the modified PI surface layer. From the molecular structure of PI, at least two distinct absorption bands associated with C-H out-of-plane bending vibration of aromatic rings could appear in the spectrum. The absorption band at 825 cm^{-1} can be assigned to a band associated with C-H vibration of aromatic rings directly bonded to carbonyl groups (1,2,4-substituted benzene ring).[23] In addition, similar to an absorption band at 725 cm^{-1} in the PET spectrum, the absorption band at 733 cm^{-1} can be assigned to a C-H vibration of oxydianiline derivative (probably 1,4-substituted benzene). According to the difference in IR absorption spectra of maleimide and phthalimide,[24] absorption bands at 486, 498, 523, and 548 cm^{-1} seem to be associated with other vibrations of aromatic rings of PI. As a result, it is suggested that the modified PI surface after ablation is mainly composed of aromatic rings. From the XPS studies, we have found a significant decrease in the atomic ratios (both oxygen to carbon and nitrogen to carbon) of PI surfaces remaining after 248-nm laser ablation.[16] As suggested by Yeh[25] from the etch product analysis for the ablation of PI, the primary cleavage reaction induced by laser irradiation is believed to be the rupture of imide rings.

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Registry No. Lumirror, 25038-59-9; Upilex-S, 32197-39-0.

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Molecular Modeling of Polymers. 7. Ab Initio Demonstration of Torsional Angle Cooperativity in Linear Chains by Molecular Dynamics

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Cooperativity is a concept often invoked to explain physicochemical processes in macromolecular systems. Most notably, transition processes of macromolecules have been described in terms of cooperative behavior among the degrees of freedom of the macromolecules. The success of the Ising model[1] in characterizing helix-coil transitions illustrates the utility of the concept of cooperativity in polymer science. Still, the ab initio demonstration that cooperative behavior is intrinsic to high molecular weight linear molecules has remained elusive. We believe that we may have come upon evidence of cooperative behavior as part of a molecular dynamics (MD) simulation of the β-orthorhombic (β_o) to α-hexagonal (α_h) transition in the C_{21} n-alkane crystals.[2]

The full details of the MD simulation will be given later, but a brief description follows. A total of 12 21-carbon chains were placed in each of two layers of the β_o

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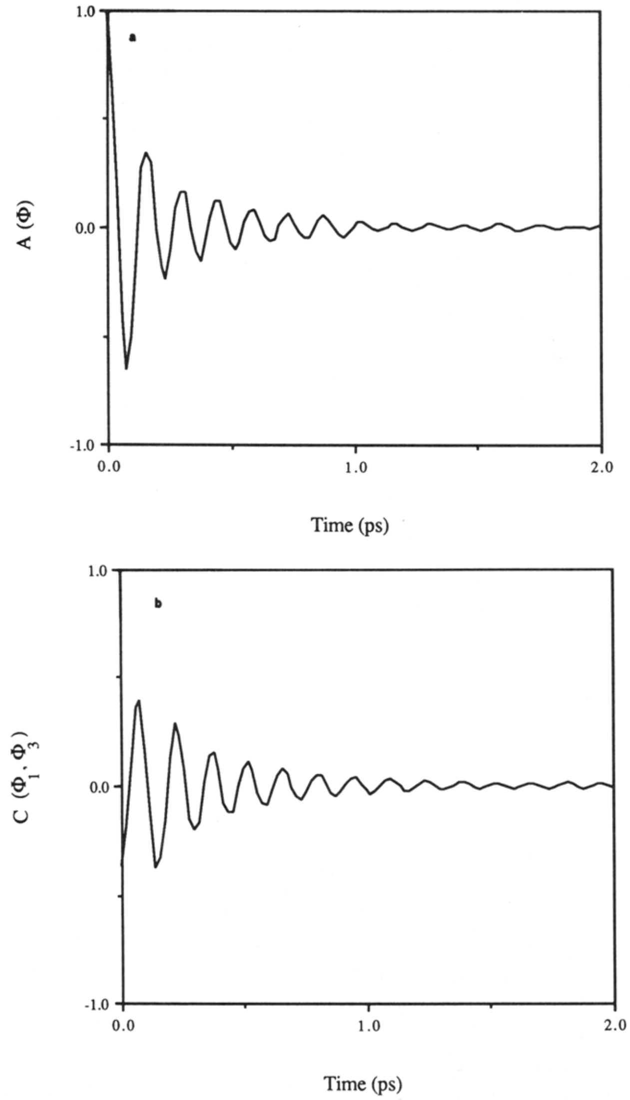

Figure 1. (a) Autocorrelation function of all torsion angles, averaged over all time. (b) Cross-correlation function of (1,3) torsion angle pairs.

paraffin bilayer crystal structure. The model includes explicit hydrogen atoms. Following a period of equilibration of the β_o structure, MD simulations, using a loose coupling (τ = 0.1 ps) to a temperature bath at 305 K,[3] were performed on a consecutive series of six microstates for 5 ps each. Changes in the unit cell cross-sectional area were varied linearly over the microstates to simulate a quasistatic volume expansion from the β_o to the α_h unit cell geometry. The chain axis dimension remained constant as in a previous alkane MD simulation.[4] Full Cartesian MD simulation, as opposed to Brownian dynamics (BD), was performed using the MM2[5] force field, with the last point in each trajectory serving as the starting point for the next microstate in the β_o to α_h pathway. Minimum image periodic boundary conditions were used to simulate the crystal.

Visual analysis of a "movie" representing the MD trajectories of the C_{21} microstates indicated periodic, wavelike motions within the chains. This periodic motion became more pronounced as the α_h unit cell geometry was approached. The MD trajectories were analyzed for evidence of cooperativity between individual torsional motions in the alkane chains.

Figure 1a displays the autocorrelation function of all torsion angles averaged over all 24 chains, and Figure 1b, the (1,3) torsion angle pair cross-correlation function for all chains, over the entire 30-ps trajectory. The autocorrelation function shows that the individual torsional motions are periodic, while the cross-correlation function indicates strong reverse coupling between (1,3) torsion angle pairs. Both the autocorrelation and (1,3) cross-correlation functions persist for about 1 ps (within 3 standard errors of the data). According to Figure 1b, when one torsion angle rotates in one direction, the other torsion angle of the (1,3) pair shows a tendency to rotate in the opposite direction. A probable consequence of such behavior is "kink"[6] formation of the type (g+/− tg−/+). This cooperative behavior is consistent with the findings of Helfand[7] and co-workers who inferred a (1,3) torsion angle pair cooperativity from statistical measures of torsion angle motions over "long" time scales (nanoseconds) using Brownian dynamics.

Very little coupling is seen in the (1,2) torsion angle pair cross-correlation function. Moderate cooperative coupling is observed in the (1,4), (1,5), and (1,6) torsion angle pair cross-correlation functions. However, these couplings are much smaller than those for the (1,3) torsion angle pairs.

Figure 2 is a digitized plot of the matrix of the 18 torsion angles of one 21-carbon chain (vertical axis) versus time (horizontal axis). The darker blocks in angle–time space indicate a positive deviation from the trans state (180°); lighter blocks indicate values below trans. It can be seen that there exist diagonal lines of near-constant shading, that is, torsion angle deviations from trans, running from left to right. Two pronounced dark diagonals and three pronounced light diagonals can be seen to start at the top of the plot near 0.6–0.8 ps and end at the bottom of the plot near 1.0–1.2 ps. Where such shaded bands exist, the plot suggests that a short time after one torsion angle reaches a maximum or minimum in its oscillation, the angle adjacent to it will do so also; and this behavior is repeated down the length of the chain. Thus, Figure 2 demonstrates that wavelike motions are propagated within the alkane chains, probably as a conse-

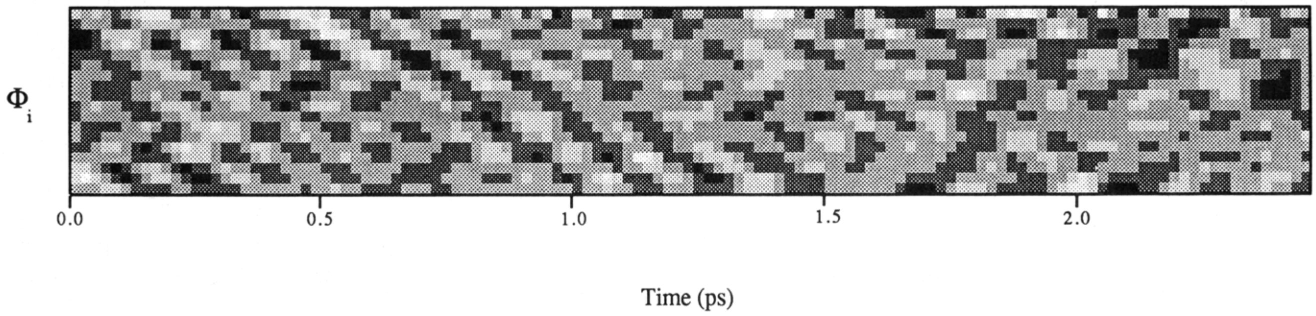

Figure 2. Digitized representation of the matrix representing the trajectories of adjacent torsion angles (of one molecule) versus time. Each gray shade represents approximately 12 deg; the values range from 152 to 213 deg.

quence of the (1,3) torsion angle pair cooperativity. Similar cooperative behavior was noticed in many other chains also.

It is possible to estimate a wave velocity of about 4700 m/s from the slope of the diagonals in Figure 2. We note that this is on the order of magnitude of the sound velocity through various crystalline media. Therefore, we believe that these motions may be related to the damped torsional oscillator (DTO) model, which has been used to explain acoustic relaxation data in alkane liquids.[8]

In conclusion, we believe that these findings from full Cartesian MD demonstrate the ab initio existence of torsion angle cooperativity. We expect that this cooperativity may be a very important factor in the structural phase transitions that take place in these materials.

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Study of the Initiation of Cationic Polymerization by Trimethylsilyl Esters

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Introduction

Protonic acids such as triflic acid are effective initiators in the cationic polymerization of vinyl[1] and oxacyclic[2] compounds. We speculated that contributing factors to the complex kinetics often observed were the complicated dissociation equilibria of the acid, hydrogen bonding, limited solubility, mixing controlled kinetics, etc. Since a trialkylsilyl group can be regarded as a bulky proton,[3] trialkylsilyl esters are expected to give clean reactions free of the complications caused by hydrogen bonding. Therefore, we recently introduced trialkylsilyl esters as a new class of initiators for cationic polymerization.[4] At the same time, another research group independently also proposed this class of compounds for the same purpose.[5]

Trimethylsilyl triflate was found to be a very active initiator for cationic polymerization but was too reactive and the polymerization could not be controlled.[4] One method of reducing the reactivity of an initiator involves the use of more nucleophilic counterions, which leads to a growing species with more covalent character, hopefully resulting in slower propagation and greater control of the molecular weight.

In this paper, we chose trimethylsilyl diphenylphosphate and trimethylsilyl methanesulfonate as the initiators to investigate the initiation of the cationic polymerization of styrene derivatives and cyclic acetals.

Results

Experimental Design. In view of the ready hydrolysis of silyl esters, particular attention was paid to possible initiation by traces of protic acids. A hindered base, 2,6-di-*tert*-butylpyridine or 2,6-di-*tert*-butyl-4-methylpyridine, was used as a probe. Introduced in the early 1980s,[6] and recently reviewed,[7] this base reacts with protic acids to form salts. The growing carbocationic chain end must not react directly with the base if its use is to be diagnostic of the initiating species. Whether it actually does or not depends on the nature of the carbocation. Bulky ones, from isobutylene or α-methylstyrene, or stabilized ones, such as trioxane, do not react. Styrene itself is more problematic, while *p*-methoxystyrene had not yet been studied.

In view of the above, to make sure the hindered base criterion was applicable, we synthesized 4-isopropenylanisole; this compound is the α-methyl-substituted analogue of *p*-methoxystyrene. Due to steric hindrance, the hindered base should not be able to abstract a proton from the derived carbocation. The reactivity of *trans*-anethole, a nonpolymerizable analogue of *p*-methoxystyrene, was also examined.

Reactions of Trimethylsilyl Diphenyl Phosphate with *p*-Methoxystyrene, Anethole, and 4-Isopropenylanisole. If ordinary polymerization conditions were used (septum-capped reaction tubes, syringes, and nitrogen atmosphere), trimethylsilyl diphenyl phosphate initiated the cationic polymerization of *p*-methoxystyrene in dichloromethane. The molecular weights of these polymers were high and the molecular weight distributions were broad. Terminal trimethylsilyl groups could not be

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