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Registry No. PHB (SRU), 26744-04-7; PHB (homopolymer), 26063-00-3.

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Communications to the Editor

Homo- and Heteroadduct Polymers Derived from Unsymmetric Diolefin Crystals

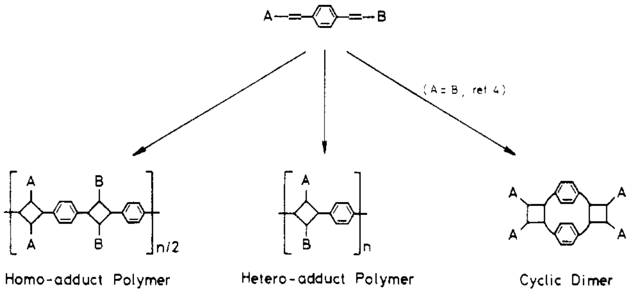
Addadi and Lahav[1,2] prepared optically active dimer and oligomers from a series of α-cyano-1,4-phenylenediacrylic ester crystals via a topochemical photoreaction. Recently, we reported that some 4-(3-oxo-3-phenyl-1-propenyl)cinnamate and 1,4-phenylenediacrylate derivatives photopolymerize into crystalline linear polymers with high molecular weight in high yields.[3] According to previous results,[1-4] various types of photoadducts, including homo- and heteroadduct polymers or cyclic dimer, can be anticipated from the topochemical reaction of unsymmetrically substituted diolefinic compounds as shown in Scheme I. More recently, we found a series of photoreactive crystals of 4-[2-(2- or 4-pyridyl)vinyl]cinnamate derivatives.

In the present communication, we report the photopolymerization behavior of two diolefin derivatives: methyl 4-[2-(4-pyridyl)vinyl]cinnamate (1) and ethyl α-cyano-4-[2-(4-pyridyl)vinyl]cinnamate (2).[5]

Fine crystals of 1, recrystallized from methanol (mp 149 °C), were dispersed in water–ethanol (9:1 volume ratio) and, with stirring, irradiated with a 500-W high-pressure mercury lamp through a uranium filter under a nitrogen atmosphere at room temperature for 13 h.

The IR spectrum of the photoproduct showed the disappearance of the carbon–carbon double bond (1630 and 975 cm^{-1}) and a shift of the carbonyl group to higher wavenumber (1710 → 1730 cm^{-1}), indicating the formation of saturated ester. In the ^{1}H NMR spectrum, olefinic peaks were absent and four new broad signals were observed at δ 3.10, 4.35, 6.9–7.1, and 8.15. The broad peak at δ 4.35 (4 H) is characteristic of protons bonded to a cyclobutane, and other peaks at δ 3.10, 6.9–7.1, and 8.15 are assigned to methoxy protons (3 H), protons at the 3- and 5-positions of 4-pyridyl (2 H) and 1,4-phenylene (4 H), and protons at the 2- and 6-positions of 4-pyridyl (2 H), respectively.

Scheme I



Comparing these spectroscopic data with those of other cyclobutane-containing polymers,[6] we assign the photoproduct to linear polymer 3 with recurring cyclobutane and aromatic rings alternating in the main chain. From the continuous change of the X-ray diffraction pattern during the reaction, the monomer crystal was gradually transformed into a nearly amorphous polymer. Although the final photoproduct is amorphous, it is obvious that the polymer is produced under topochemical control because a single configuration of the cyclobutane is formed exclusively.

Polymer 3 had an inherent viscosity of 0.47 dL/g at 0.30 g/dL in *m*-cresol at 30 °C and was soluble in *N*,*N*-dimethylformamide, dimethyl sulfoxide, and strong acids such as concentrated HCl, indicating electrolyte character of the polymer chain.

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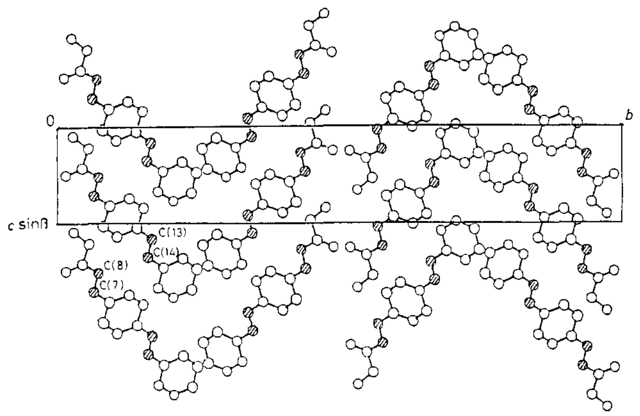
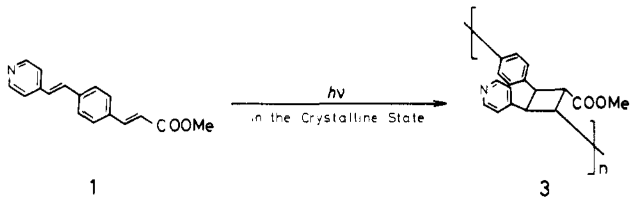


Figure 1. Crystal structure of 1, viewed along the *a* axis. The atoms comprising the ethylenic groups are hatched for clarity.

Scheme II



The crystal structure of 1, viewed along the *a* axis is shown in Figure 1.[7]

From the crystal structure it is concluded that on irradiation, two nonequivalent double bonds in crystal 1 react to give a linear heteroadduct racemic polymer in which a cyclobutane ring is in the 1,3-*trans* configuration (Scheme II).

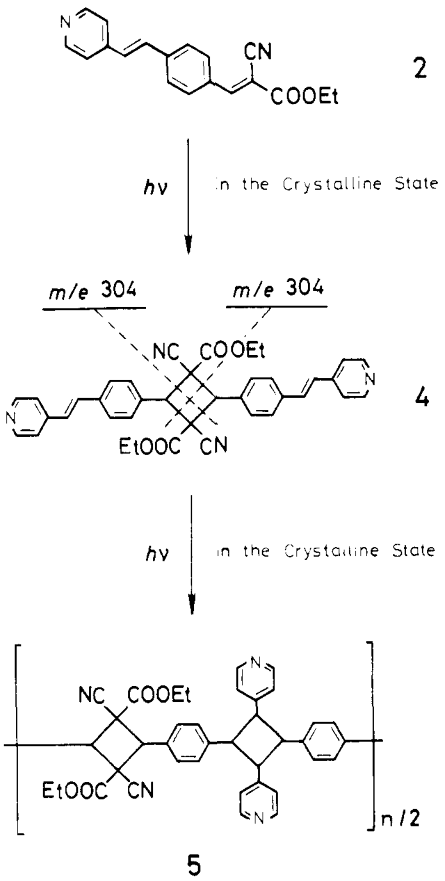
The intermolecular reactive double bonds, separated by 4.023 (9) Å for C(7)⋯C(14) and 4.097 (10) Å for C(8)⋯C(13), are nonparallel while these distances are within those of normal reactive bonds. Topochemical [2 + 2] photodimerization of the double bonds oriented nonparallel has been reported for several olefinic crystals in recent papers.[4,8]

On photoirradiation in the same manner as crystal 1, crystal 2 was found to be highly reactive in the crystalline state; however, in contrast with crystal 1, crystal 2 gave a linear homoadduct polymer 5. Polymer 5 had an inherent viscosity of 0.36 dL/g at 0.30 g/dL in chloroform at 30 °C and was soluble in ordinary organic solvents and aqueous acidic solutions such as aqueous HCl and H_2SO_4 solutions. At the early stage of the photoreaction, only one type of dimer was isolated in fairly high yield (54.2%). From IR, NMR, and mass spectroscopies, the dimer was confirmed to be 4 (diethyl 1,3-dicyano-2,4-bis[4-[2-(4-pyridyl)vinyl]phenyl]-1,3-cyclobutanedicarboxylate).[9] No trace of another dimer, 1,3-bis[4-[2-cyano-2-(ethoxycarbonyl)vinyl]phenyl]-2,4-bis(4-pyridyl)cyclobutane, was detected at any of the reaction stages, indicating exclusive formation of 4 as an intermediate dimer. This implies that the growing species consist of even-number degree of polymerization during the entire course of polymerization, which was confirmed by GPC analysis.

$$\mathrm{M} + \mathrm{M} \xrightarrow{h\nu} \text{dimer (M–M)} \xrightarrow{h\nu} \text{polymer } (\mathrm{M–M})_{n/2}$$

Crystal 4, recrystallized from ethanol, shows essentially the same crystal diffraction pattern with the crystal as prepared but on photoirradiation, gives a higher molecular weight polymer 5 ($\eta_{\text{inh}} = 0.36$ dL/g $\rightarrow \eta_{\text{inh}} = 0.64$ dL/g). According to X-ray diffraction analysis, the photoproduct at the inital stage (after irradiation for 5 h) is crystalline and then progressively becomes amorphous with further polymerization. 2 crystallizes in the triclinic crystal system, space group $P\bar{1}$, with a = 11.664 (4) Å, b = 9.151 (3) Å, c = 7.814 (2) Å, α = 85.84 (3)°, β = 104.44 (4)°, γ = 80.05 (2)°, V = 789.7 Å^3, D_x = 1.279 g cm^{-3}, Z = 2, and R = 0.082.

Scheme III



The crystal structure of 2 is shown in Figure 2.

In crystal 2, every molecule is related to its neighboring molecules by two different centers of inversion along the stack direction. The two pairs of equivalent double bonds are separated by a distance of 3.758 and 4.878 Å, respectively. As the former distance is within the conventional reactive one while the latter is much longer than the reactive one, the probable dimerization occurs between the double bonds with the distance of 3.758 Å. We cannot discuss any details of the behavior of dimer 4 without crystallographic analysis, which is now in progress.

Consequently, under topochemical control crystal 2 gives a linear homoadduct polymer 5 via intermediate dimer 4. The overall reaction scheme of crystal 2 is presented in the Scheme III.

In conclusion, crystals 1 and 2 give a new type of hetero- and homoadduct polymers, 3 and 5, respectively, having the cyclobutane ring in the 1,3-trans configuration in the main chain via a topochemical process. Crystal 2 passes through intermediate dimer 4 exclusively in the course of photopolymerization. Such a remarkable difference of photochemical behavior in these two crystals, having extremely similar chemical structures, cannot be explained by their intrinsic chemical reactivity but should arise from the difference in molecular arrangement in the crystals.

In addition to the electrolytic property of 3 and 5 it is of further interest that one side of the rigid polymer chain in as-prepared 3 is hydrophilic and the other is hydrophobic under restricted rotation of the σ-bond in the main

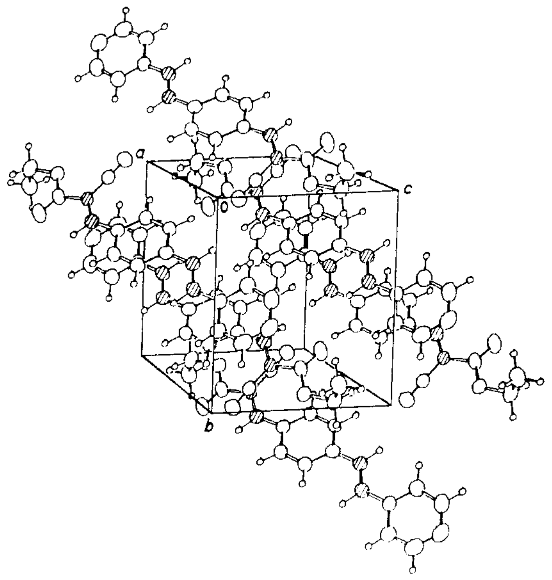


Figure 2. Crystal structure of 2. The atoms comprising the ethylenic groups are hatched for clarity.

chain. On the other hand, 5 consists of a hydrophilic and hydrophobic alternating structure in the polymer chain.

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Registry No. 1 (homopolymer), 100515-61-5; 2 (homopolymer), 100515-63-7; 4, 100515-64-8.

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(9) Dimer 4: mp 189.5-192.0 °C; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.95 (t, 6H), 4.03 (q, 4 H), 5.13 (s, 2 H), 6.9-7.7 (m, 16 H), 8.55 (d, 2 H); mass spectrum, m/e 608 (P), 304 (P/2, symmetric cleavage of the cyclobutane ring), but no trace of asymmetric cleavage of the cyclobutane ring.
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Configurational Diffusion in Semidilute Solutions[†]

The viscoelastic properties of entangled polymeric fluids are inextricably linked to the dynamics of single chains, yet there are relatively few measurements of these single-chain dynamics, since most experimental methods are sensitive to the relatively rapid collective fluctuations of many-chain systems. For this reason, experimental methods which focus on single-chain properties often employ some sort of labeling technique. In this Communication we report measurements of the single-chain dynamics of polystyrene (PS) in a poly(vinyl methyl ether) (PVME)/toluene host. In these experiments the semidilute PVME solutions are index matched by the solvent (and hence give no measurable scattering), whereas the dilute high molecular weight PS scatters very strongly. Using this "optically" labeled-chain technique[1] we were able to observe the diffusion of long-wavelength, single-chain modes in semidilute solutions and thus test current ideas about the semidilute screening of hydrodynamic interactions.

Although detailed theories exist for the internal modes of polymer chains,[2,3] it is convenient here to give a description in terms of scaling ideas.[4] The important parameter in a dynamic light scattering experiment is q, the momentum transfer. In terms of λ, the wavelength in the scattering volume, and θ, the scattering angle, $q = 4\pi \sin(\theta/2)/\lambda$, which has the dimensions of inverse length. A dynamic light scattering experiment measures the relaxation times of fluctuations which occur on a length scale $1/q$. In the simplest experiments these fluctuations may be due to translational diffusion of a narrow fraction polymer, in which case a single relaxation time is measured, $1/D_tq^2$, which is the mean time for a polymer with diffusion constant D_t to diffuse a distance $1/q$. However, when the length scale $1/q$ is smaller than R, the radius of the polymer, internal degrees of freedom contribute to the observed relaxation processes if the polymer is in a fluctuating (nonglobule) state. In this fluctuating state each of the normal modes of a polymer has a relaxation time which is proportional to R^2/D_t times some function of the mode index. So if we consider a transformation of scale, $R \rightarrow R'$, the relaxation time of the pth mode will become $\tau_p(R') = \tau_p(R)(R'/R)^{2+\alpha}$, where α is the diffusion exponent defined by $D_t \sim R^{-\alpha}$. Now a mode of spatial extent R will have fluctuations, δR, of magnitude R, so we may replace R by $1/q$ to obtain $\tau_q \sim 1/q^{2+\alpha}$ for the q dependence of the relaxation time. The Rayleigh line width, or mean relaxation rate, Γ, is just $1/\tau_q \sim q^{2+\alpha}$.

In dilute solution there are two possibilities for the diffusion exponent α, corresponding to strong or weak hydrodynamic interactions. If hydrodynamic interactions are strong the diffusion is Stokes-Einstein, giving $(T/\eta_0)R^{2-d}$ for the diffusion coefficient in terms of the temperature, solvent viscosity, and dimension of space, respectively. In the regime $qR \gg 1$ this gives

$$\Gamma \sim \frac{T}{\eta_0} q^d \tag{1}$$

which we simply call Zimm behavior.[5] Zimm dynamics have been observed by several investigators.[6-8] On the other hand, if hydrodynamic interactions are weak the diffusion coefficient is T/f, where $f = Nf_0$ is the friction factor for the chain of N monomers and f_0 is the monomeric friction factor. In this case $D_t \sim R^D$, where D is the fractal dimension, and

$$\Gamma \sim \frac{T}{f_0} q^{2+D} \tag{2}$$

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