(br, 2 H, OH and COOH), 7.49 (d, 1 H, J = 7.5 Hz, NH).

Without further purification, the above solid (600 mg, 2.2 mmol) was dissolved in acetone (80 mL), and to this solution was added *p*-chlorophenacyl bromide (520 mg, 2.2 mmol) and KHCO₃ (230 mg, 2.3 mmol). The mixture was heated at reflux for 3.5 h. The hot solution was filtered, and the filtrate was concentrated to give a brown oil. The crude product was purified by low-pressure column chromatography (hexane–ethyl acetate, 80:20 to 50:50) to provide **3** (810 mg, 87%) as an oil: TLC R_f (solvent B) 0.43; $[\alpha]^{23}_D$ −19.1° (*c* 1.3, CHCl₃); NMR (CDCl₃) δ 0.78 [d, 3 H, J = 6.9 Hz, CH(C*H*₃)₂], 0.97 [t, 6 H, CH₂CH(C*H*₃)₂], 1.08 [d, 3 H, J = 6.9 Hz, CH(C*H*₃)₂], 1.75 [m, 3 H, C*H*₂C*H*(CH₃)₂], 2.20 [m, 1 H, C*H*(CH₃)₂], 3.61 (q of AB pattern, 2 H, J = 15.3 Hz, COCH₂CO), 3.74 (d, 1 H, OH, J = 5.1 Hz), 4.13 (d, 1 H, J = 3.0 Hz, OCHCO), 4.74 (m, 1 H, NHC*H*), 5.26 and 5.42 (q of AB pattern, 2 H, J = 16.5 Hz, OCH₂CO), 7.28 (d, 1 H, J = 8.1 Hz, NH), 7.46 and 7.83 (2 dd, 4 H, J = 6.6 Hz, phenyl); ¹³C NMR δ 15.3, 19.6, 21.5, 22.9, 24.8, 30.9, 40.9, 45.9, 50.9, 66.2, 81.3, 128.9, 129.1, 131.9, 140.3, 165.1, 171.8, 190.2, 207.7. Anal. Calcd for C₂₁H₂₈NO₆Cl: C, 59.22; H, 6.58; N, 3.29. Found: C, 59.12; H, 6.62; N, 3.18.

***N*-[(*S*)-4-Hydroxy-5-methyl-3-oxohexanoyl]-L-leucine (20) from 15.** To a stirred slurry of KO-*t*-Bu (30 g, 260 mmol) at room temperature in ethyl ether (150 mL) was added water (1.5 mL, 83 mmol). After 5 min, a solution of **15** (4.9 g, 13.2 mmol) in ethyl ether (100 mL) was added. After the mixture was stirred for 40 h at room temperature, water (40 mL) was added, and the resultant mixture was extracted with saturated NaHCO₃ (3 × 30 mL). The aqueous extracts were acidified (pH 2) and extracted with ethyl acetate (3 × 100 mL), and the organic extracts were dried (Na₂SO₄) and concentrated to give an oil. The crude product was purified by low-pressure column chromatography (chloroform–acetone, 80:20) to provide **20** (2.37 g, 70%) as a pale yellow solid: NMR showed the product to exist as an epimerized form in 70:30 ratio.

(2*SR*, 4*S*)-4-(2,2,2-Trimethylacetoxy)-2,5-dimethyl-3-oxohexanoic Acid *tert*-Butyl Thio Ester (21). Anhydride **4g** (3.6 g, 12.7 mmol) in THF (10 mL) was treated with lithium *tert*-butyl thiopropionate (25 mmol) in THF (20 mL) at −72 °C following the usual procedure. Purification by low-pressure column chromatography (hexane–ethyl acetate, 95:5) furnished **21** (2.2 g, 54%): TLC R_f (solvent A) 0.85; NMR (CDCl₃) δ 0.88–1.1 [set of m, 6 H, CH(C*H*₃)₂], 1.27 [2 s, 9 H, C(CH₃)₃], 1.33 and 1.38 (2 d, 3 H, J = 6.9, 7.3 Hz, CHC*H*₃), 1.47 [2 s, 9 H, C(CH₃)₃], 2.37

[m, 1 H, C*H*(CH₃)₂], 3.82 and 3.91 (2 q, 1 H, J = 6.6, 7.2 Hz, C*H*CH₃), 5.05 and 5.10 (2 d, 1 H, J = 3.0, 4.2 Hz, OCHCO); assigned as 58:42 ratio of diastereomers.

***N*-[2*SR*,4*S*]-4-(2,2,2-Trimethylacetoxy)-2,5-dimethyl-3-oxohexanoyl]-L-leucine Methyl Ester (22).** Compound **22** was obtained by the usual manner as described above from **21** (600 mg, 1.82 mmol) and Cl⁻H₂⁺-Leu-OMe (330 mg, 1.82 mmol) as a yellow oil in 76% yield after purification by low-pressure column chromatography (hexane–ethyl acetate, 95:5): TLC R_f (solvent A) 0.48; $[\alpha]^{23}_D$ − 2.28 (*c* 1.01, CHCl₃); NMR (CDCl₃) δ 0.87–1.10 [set of m, 12 H, CH(CH₃)₂ × 2], 1.27 [s, 9 H, C(CH₃)₃], 1.37 and 1.49 (2 s, 3 H, J = 7.5, 6.9 Hz, ratio 51:49, CHC*H*₃), 1.60 [m, 3 H, C*H*₂C*H*(CH₃)₂ in leucine], 2.30 [m, 1 H, C*H*(CH₃)₂], 3.66 (q, 1 H, J = 7.5 Hz, C*H*CH₃), 3.71 and 3.73 (2 s, 3 H, OCH₃, ratio 50:50), 4.53 (m, 1 H, NC*H*CO), 4.91 and 5.07 (2 d, 1 H, J = 3.3, 3.6 Hz, ratio 52:48, OCHCO), 6.90 (2 d, 1 H, NH); assigned as 1:1 ratio of diastereomers. Anal. Calcd for C₂₀H₃₅NO₆: C, 62.34; H, 9.09; N, 3.64. Found: C, 62.12; H, 9.14; N, 3.74.

Influence of the Solvent on the Nature of a Diradical Tetramethylene Intermediate

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In the spontaneous thermal reactions of *p*-methoxystyrene and methyl 3,3-dicyanoacrylate, several reaction products are observed: a 1/1 alternating copolymer, a double Diels–Alder adduct, and the cyclobutane adduct. In dipolar aprotic solvents, no polymerization occurs, and the double Diels–Alder adduct is favored, while in protic polar solvents cyclobutane formation competes with copolymerization. In nonpolar solvents, copolymerization dominates. A diradical tetramethylene intermediate is proposed as the key intermediate. In polar solvents, this diradical exhibits considerable polar character, and Coulombic attraction between the termini favors the coiled or gauche conformation, leading preferentially to cycloadducts. In nonpolar solvents, the trans conformation initiates the polymerization. The main factors influencing the products are the solvent polarity and the ability of the solvent to interact with the diradical tetramethylene.

During our continuing study of the spontaneous reactions of electron-poor olefins with electron-rich olefins, we have proposed the Bond-Forming Initiation Theory, as a unifying concept for all the observed products.[1] Both polymers and small molecule addition products have been

observed in these reactions. The key intermediate in all these reactions is a tetramethylene intermediate, which can be predominantly zwitterionic or diradical in nature. This tetramethylene can then form the cycloadduct or initiate polymerization.

With extremely electron-rich and electron-poor olefins, a zwitterionic intermediate is formed, as witnessed in many cases by the cationic homopolymerization of the donor

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(1) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 440.

Table I. Effect of the Solvent on the Product Distribution[a]

solvent	double Diels–Alder	cyclobutane adduct	oligomer	copolymer	combined polymer	molecular weight	time to fade, h
DMSO	93	7	0	0	0		
DMAC	90	10	0	0	0		
sulfolane	90	10	0	tr	0		
γ-butyrolactone	92	8	0	0	0		
CH_3COOH	97	3	0	0	0		2
HFIP	0	73	0	27	27	60000	1
MeOH	0	71	0	29	29		
CH_3CN	23	35	0	42	42	50000	5
EtOH	0	50	0	50	50	60000	1
CH_3NO_2	0	56	0	44	44	50000	1
t-BuOH	21	33	0	46	46	30000	1
acetone	39	5	0	56	56	50000	10
toluene	42	0	1	57	57	40000	1
THF	25	8	8	59	67	40000	10
benzene	30	tr	0	70	70	45000	1
$CHCl_3$	8	14	10	68	78	60000	2
$(CH_2Cl)_2$	4	8	2	86	88	40000	2
CCl_4	0	0	54	46	100	25000	1
EtOAc	0	0	26	74	100	50000	5

[a] Conditions: All reactions are run at 1 M in each olefin at 28 °C for 20 h. The yields in the table are percent yield calculated on the basis of MDA. The combined polymer yield is the sum of the oligomers and the precipitated polymer. The molecular weights were determined by SEC (see the Experimental Section). "Time to fade" is the time for the yellow EDA color to disappear.

olefin, for example if *N*-vinylcarbazole is used.[2] Cyclobutane adducts, which are also formed in these reactions, can revert back to the tetramethylene and thus are able to initiate the cationic polymerization of excess donor olefin. The zwitterionic intermediate can be trapped in methanol, as has been shown for the reactions of vinyl ethers with tetracyanoethylene among many other examples.[3,4]

As we shift to less electron-rich and electron-poor olefins, diradical tetramethylene intermediates occur, which are able to initiate radical alternating copolymerization of the two olefins. Kinetics and trapping experiments support this hypothesis.[5]

In the present study, we investigated a case on the borderline between the two extreme cases described above. A relatively electron-rich olefin, *p*-methoxystyrene (*p*-MeOSt) was chosen as the donor olefin. Methyl 3,3-dicyanoacrylate (MDA) was chosen as the electron-poor olefin because two cyano substituents on one carbon are known to effectively stabilize a negative charge. From previous preliminary studies, it was known that this olefin pair spontaneously copolymerizes in dichloroethane, which indicates that the tetramethylene intermediate has diradical character.[6] Huisgen,[4] along with theoretical chemists,[7,8] has postulated that the diradical and zwitterionic tetramethylenes are hybrids and that there is through-bond interaction between the two terminals. The question then is if different conditions will affect the behavior of the diradical tetramethylene intermediate in the reactions of *p*-methoxystyrene and methyl 3,3-dicyanoacrylate and possibly if we can make it switch to a zwitterion. Very little or no literature could be found on this subject. One report by Reinhoudt discusses the influence

of the polarity of the solvent on the product in the case of a zwitterionic tetramethylene intermediate.[9]

Results

Identification of Reaction Products. The reactions of *p*-methoxystyrene (*p*-MeOSt) and methyl 3,3-dicyanoacrylate (MDA) were run in equimolar amounts at room temperature under argon atmosphere in a series of solvents. The results are summarized in Table I. Upon mixing these two olefins, the expected yellow color of the electron donor–acceptor (EDA) complex appeared. The reaction time necessary for complete conversion could be deduced from disappearance of this color, except in the cases of the highly dipolar solvents, in which complexation of the solvent to the electron-poor olefin MDA led to dark brown solutions.

The polymer can be precipitated in ether, and the yield is determined gravimetrically. The composition of the remaining material was determined by size-exclusion chromatography (SEC) with a low molecular weight column, which separates compounds in the molecular weight range of 1000 down to 200. Several of the cycloadducts that are formed in these reactions decompose on silica gel columns, and the SEC offers a very convenient and mild method to identify these compounds. Three different peaks could be observed in the size-exclusion chromatogram depending on the reaction conditions. In some solvents, only one peak was observed; this product could then be purified and analyzed. The compounds were all identified by 250-MHz ^1H NMR, IR, and chemical analyses.

One cycloadduct was found to be very insoluble in most common organic solvents, except in acetone. It even crystallized out of dimethyl sulfoxide and dimethyl acetamide. This compound proved to be a 2/1 adduct of MDA and *p*-MeOSt, on the basis of chemical analysis. NMR and IR spectroscopy indicated that it is the double Diels–Alder adduct. Two isomers **1a** and **1b** are present in a 80/20

(2) Gotoh, T.,; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.

(3) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

(4) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.

(5) Hall, H. K., Jr.; Padias, A. B.; Pandya, A.; Tanaka, H. *Macromolecules* **1987**, *20*, 247.

(6) Pandya, A. M.S. Thesis, University of Arizona, 1986.

(7) Hoffmann, R.; Swaminathan, S.; Odell, R. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091.

(8) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(9) Reinhoudt, D. N.; Geevers, J.; Trompenaars, W. P.; Harkema, S.; Van Hummel, G. J. *J. Org. Chem.* **1981**, *46*, 424.

Scheme I[a]

[a] E = COOCH$_3$.

Scheme II

gauche conformation in polar solvents   trans conformation in nonpolar solvents
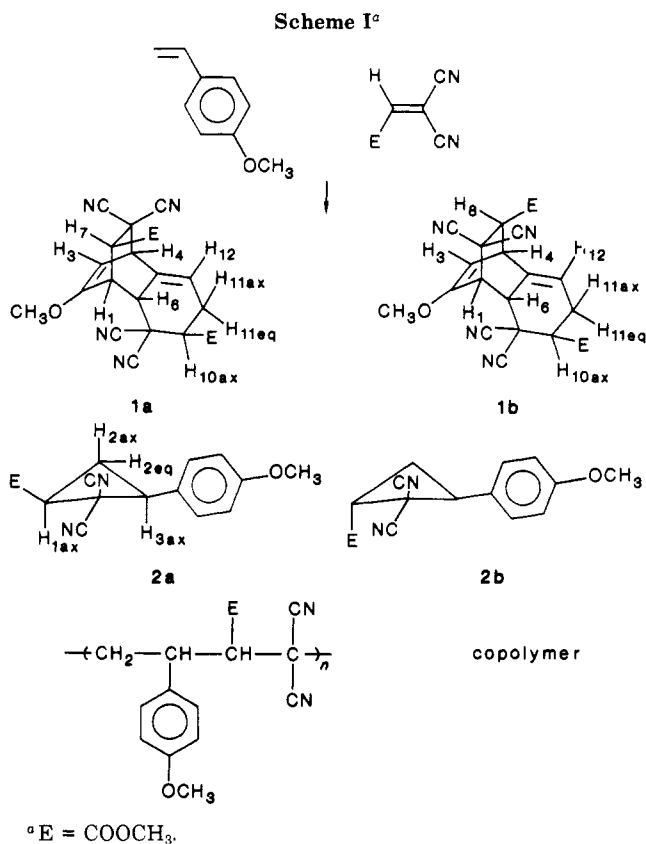
ratio, which only differ in the addition mode of the second molecule of MDA (Scheme I).

A second small molecule that is formed in these reactions is the cyclobutane adduct, which is also present as two isomers. According to the NMR spectrum of the mixture, the cis isomer **2a** is present in 3/1 ratio versus the trans isomer **2b** (Scheme I).

The third peak that can be observed in the SEC is due to oligomeric alternating copolymer. It has an infrared spectrum and chemical analysis identical with those of the copolymer. The copolymer is strictly alternating. The molecular weight of the precipitated polymers is in the 30 000–60 000 range as determined by SEC.

The yield of the polymer, given in Table I, was first determined gravimetrically. The yields for the double Diels–Alder and the cyclobutane adducts and the oligomers were then calculated from the integration of the SEC chromatograms, after calibration of the UV detector. The combined amount of polymer is considered to be the sum of the precipitated polymer and the oligomer, as both are formed by the same radical chain mechanism.

The time necessary for the yellow color of the EDA complex to disappear is also included in Table I. This gives an indication for the time necessary for all olefin to react.

Main Trends. In Table I, the solvents are listed in order of increasing combined polymer yield, which includes precipitated polymer and oligomer. The yields of combined polymer vary from 0% in the dipolar aprotic solvents to 100% in a nonpolar solvent such as carbon tetrachloride. A correlation can be observed between increasing polymer yield and decreasing polarity of the solvent.

Two different cycloadducts are formed in these reactions: in the dipolar aprotic solvents, the double Diels–Alder adduct is favored, in contrast to the polar protic solvents such as methanol and hexafluoroisopropyl alcohol (HFIP) in which only the cyclobutane adduct is observed. In the other solvents, mostly mixtures are observed of the possible products.

Discussion

In view of the results, we shall now try to find a relationship between the properties of the different solvents and the observed products; in particular, we shall discuss the influence of the solvent on the conformation of the tetramethylene.

In the more polar solvents, the diradical tetramethylene intermediate has more polar character than in the nonpolar solvents; the radical on C1 has a partial positive charge, δ^+, while the radical on C4 has a partial negative charge, δ^-. In other words, the diradical has shifted more towards zwitterionic behavior. This is possible because of the through-bond interaction between the C1 and C4 positions, as has been proposed by theoretical chemists.[7,8] Salem and Rowland regard the diradical and zwitterionic tetramethylene as resonance structures. In their view, the nature of the tetramethylene is determined by the substituents at the terminal centers. We now advance the theory that in a borderline case such as the one under study, the medium can also shift the nature of the tetramethylene.

Due to Coulombic attraction, the more polar diradical in polar solvents has a larger tendency to stay in the coiled or gauche conformation than the same diradical tetramethylene in a nonpolar solvent. In a nonpolar solvent, rotation around the central C2–C3 bond to form the trans conformer should be easier due to reduced Coulombic attraction, and thus more of this trans conformer will be present (Scheme II). We have postulated that this trans tetramethylene is the true initiating species of the radical alternating copolymerization[5] because the steric constraints of monomer approach to the gauche conformation are just too great. Therefore, less or no polymer will be formed in the more polar solvents, which is observed. In Table I, the solvents are listed in the order of increasing total polymer yield obtained, and this corresponds to roughly the order of decreasing polarity.

There is a distinction between the aprotic and the protic polar solvents in the nature of the small molecule that is formed in these solvents: in aprotic solvents the Diels–Alder adduct is favored, whereas only the cyclobutane adduct is formed in the protic solvents. The first addition to form the double Diels–Alder adduct in these reactions is believed to proceed by a stepwise mechanism (the second addition most probably occurs as a concerted reaction in classical [4 + 2] fashion). A similar stepwise mechanism and product in a [4 + 2] addition has been observed in our trapping experiments in the reaction of p-MeOSt with dimethyl cyanofumarate, in which a radical also attacked the ortho position of a phenyl substituent to form a six-membered ring. These double Diels–Alder adducts on styrene derivatives have been reviewed by Wagner-Jauregg[10], and we have identified such adducts previously in the reactions of, for example, carbomethoxy- and dicarbomethoxymaleic anhydride with p-MeOSt.[11,12] If we

(10) Wagner-Jauregg, T. *Synthesis* 1980, 769.

assume that the diradical tetramethylene is the intermediate for the formation of both the Diels–Alder adduct and the cyclobutane adduct, then the solvent must play a crucial role in determining which product is formed.

Dipolar aprotic solvents, such as dimethyl sulfoxide, are very efficient at stabilizing a positive charge or partial charge, as the δ^- end of the dipole of the solvent molecule is very exposed. They are, however, not able to stabilize a negative charge. This means that the δ^+ radical end of the tetramethylene diradical is surrounded by DMSO. The δ^- end, though, is free, and a very small rotation of the C2–C3 bond of the tetramethylene brings it in very close proximity to the ortho position of the phenyl ring, and the radical will be much more stabilized in the phenyl ring. Combination of the two radicals forms the exo double bond. Concerted addition of the second MDA molecule can then take place at the cyclohexadiene moiety of the molecule.

In a protic solvent such as methanol, though, both the δ^+ and δ^- radicals will be stabilized by the solvent, which means that this diradical will be more heavily solvated. In this case, cyclobutane formation will be favored, as the steric hindrance from the solvent molecules will prevent rotation of the phenyl group.

This tendency holds up in less polar solvents, too, although not as rigorously. In ethanol and nitromethane, only the cyclobutane adduct is formed, while in toluene and benzene, only the double Diels–Alder adduct is obtained. The only exception is acetic acid: the major product is the double Diels–Alder adduct, and very little cyclobutane is formed, but acetic acid is a nonpolar (ϵ = 6.15), protic solvent that forms dimers.

In the cycloaddition of vinyl ethers to tetracyanoethylene, the zwitterionic tetramethylene is trapped if the reaction is run in methanol.[3] The reaction of MDA with vinyl ethers leads exclusively to the cyclobutane adduct, and in this reaction, too, methanol is able to trap the tetramethylene intermediate, confirming its zwitterionic nature.[13] No trapping occurs in the case of *p*-MeOSt and MDA, which leads us to believe that although this diradical tetramethylene exhibits polar properties, it is not a true zwitterionic tetramethylene.

There is no correlation with the reaction time as determined by the disappearing color of the EDA complex. This is probably due to the fact that cycloaddition reactions are favored in the polar solvents, in which we would expect faster reaction, but the polymerization, which is a chain reaction, is favored in the nonpolar solvents.

Conclusion

The tetramethylene intermediate formed in the reactions of *p*-methoxystyrene and methyl 3,3-dicyanoacrylate is a diradical, although it is highly polarizable. The main factors influencing the product are the solvent polarity and the ability of the solvent to interact with the diradical tetramethylene. The polar character of this diradical is favored in the more polar solvents, and due to Coulombic attraction, it will exist in the coiled or gauche conformation in these solvents. On the other hand, in nonpolar solvents the trans conformation begins to compete; this conformation is able to initiate the alternating copolymerization. In our opinion, even though there is evidence for a highly polarized diradical in the polar solvents, the diradical

tetramethylene retains its diradical character and does not switch to a zwitterionic tetramethylene.

Experimental Section

General Methods. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 250-MHz WM-250 Bruker spectrometer. Chemical analyses were performed by Desert Analytics, Tucson, AZ.

Size-exclusion chromatography (SEC) was performed with Du Pont Zorbax 300S and 60S SEC columns and a IBM Type A column for the molecular weight determinations of the polymers. For the small molecule analysis, only the latter column was used. The eluent was chloroform for the polymers and acetonitrile for the small molecules. The UV detector is from Spectra-Physics and the integrator is a Hewlet-Packard 3392A instrument.

Reagents. *p*-Methoxystyrene was purchased from Aldrich and distilled over calcium hydride. Methyl 3,3-dicyanoacrylate was synthesized by a Knoevenagel reaction of methyl glyoxylate and malononitrile (distilled).[14] The solvents were purified by standard procedures.

Reaction Procedure. Under argon atmosphere and in a capped tube, 1 mmol of each olefin are mixed in 1 mL of solvent. The reaction mixture is placed at room temperature, and the disappearance of the EDA color is monitored. After the reaction is complete and if necessary, the polymer is dissolved in chloroform, and the solution is added dropwise to a 10-fold excess of ether with stirring. The precipitated polymer is filtered off, dried, and weighed. The remaining solution is rotoevaporated, and the products are analyzed by SEC.

Double Diels–Alder Adduct 1a and 1b. The product was obtained from the reaction of γ-butyrolactone, from which the adduct precipitates after 2 days. The adduct was then recrystallized from ether at –45 °C. Mp: 236 °C. IR (KBr): 2953, 2253, 1755, 1636, 1432, 1392, 1345, 1253, 1227, 1019 cm^{-1}. NMR (acetone-d_6) of isomer 1a: The assignments and the coupling constants were determined by using decoupling. δ 6.06 (H$_{12}$, m), 5.21 (H$_3$, q) 4.28 (H$_4$, d) 3.83 (H$_7$, d), 3.8 (COOCH$_3$, 2 s), 3.8 (H$_{10ax}$, m), 3.60 (MeO, s), 3.49 (H$_1$, m) 3.40 (H$_6$, m), 2.98 (H$_{11ax}$, 12 peaks), 2.43 (H$_{11eq}$, 16 peaks); $J_{1,6}$ = 1–2 Hz, $J_{1,7}$ = 1.5 Hz, $J_{1,3}$ = 2.5 Hz, $J_{3,4}$ = 7.4 Hz, $J_{10ax,11eq}$ = 6.9 Hz, $J_{10ax,11ax}$ = 10.8 Hz, $J_{11ax,11eq}$ = 19.2 Hz, $J_{11ax,12}$ = 3.4 Hz, $J_{11eq,12}$ = 3.2 Hz, $J_{11ax,6} \approx J_{11eq,6} \approx J_{12,6}$ = 3.2 Hz.

The isomer 1b is only 20% of the mixture. The following features allow us to assign the structure: H$_4$ is a quartet, slightly upfield from H$_4$ in 1a (at 4.04 ppm, $J_{3,4}$ = 11.0, $J_{4,8}$ = 6.8 Hz); H$_{12}$ is shifted upfield to δ 5.96 (closer to COOCH$_3$ group); H$_3$ has a minimal shift upfield. Anal. Calcd for C$_{21}$H$_{18}$N$_4$O$_5$: C, 62.06; H, 4.46; N, 13.79. Found C, 61.77; H, 4.29; N, 13.63.

1-(*p*-Methoxyphenyl)-2,2-dicyano-3-carbomethoxycyclobutane 2a and 2b. Cyclobutane could be obtained from the reaction in methanol and was recrystallized from ether and petroleum ether at –45 °C. Mp: 111–118 °C. IR (KBr): 2960, 1739, 1612, 1514, 1439, 1257, 1203, 1177, 1030, 835 cm^{-1}. NMR (CDCl$_3$) of the cis isomer 2a: δ 4.10 (H$_{1ax}$, q), 3.87 and 3.82 (COOCH$_3$, 2 s), 3.72 (H$_{3ax}$, q), 3.00 (H$_{2ax}$, q), 2.62 (H$_{2eq}$, 2 t); $J_{1ax,2ax}$ = 11.8 Hz, $J_{1ax,2eq}$ = 8.5 Hz, $J_{2ax,2eq}$ = 11.9 Hz, $J_{2ax,3ax}$ = 11.0 Hz, $J_{2eq,3ax}$ = 8.5 Hz.

The shifts and coupling constants of the trans isomer 2b could not be determined, as this isomer only comprises 25% of the mixture. Anal. Calcd for C$_{15}$H$_4$N$_2$O$_3$: C, 66.65; H, 5.22; N, 10.37. Found C, 65.97; H, 5.06; N, 10.32.

Alternating Copolymer. The polymer is a white powder. IR (KBr): 2956, 2255 (w), 1740, 1611, 1583, 1514, 1437, 1257, 1181, 1030, 836 cm^{-1}. NMR (CDCl$_3$): δ 7.1 (br, 4 H), 3.9 (several s + br peak, 8 H), 3.0–1.0 (br, 2 H). Anal. Calcd for C$_{15}$H$_4$N$_2$O$_4$: C, 66.65; H, 5.22; N, 10.37. Found C, 66.25; H, 5.03; N, 10.25.

The spectra and the analyses of the oligomer are identical with the data obtained for the copolymer.

(11) Hall, H. K., Jr.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* **1982**, *47*, 1451.

(12) Hall, H. K., Jr.; Sentman, R. C.; Nogues, P. *J. Org. Chem.* **1982**, *47*, 3647.

(13) Padias, A. B., unpublished results.

(14) Hall, H. K., Jr.; Sentman, R. C. *J. Org. Chem.* **1982**, *47*, 4572.