Macromolecules **1993,** *26,* 6359–6363

New Dicyano-Containing Cyclopolymers Having High Stereoregularity Derived from Dimethacrylmalononitrile

Takashi Tsuda and Lon J. Mathias*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

Received July 14, 1993; Revised Manuscript Received September 7, 1993[⊗]

ABSTRACT: New monomers for cyclopolymerization were synthesized through phase transfer catalyzed reaction between methyl or ethyl α-(chloromethyl)acrylate and malononitrile. The dicyano-containing diacrylates obtained undergo AIBN-initiated or spontaneous thermal polymerization in bulk to give soluble cyclopolymers with virtually complete cyclization (cyclization efficiency $f_c > 0.99$) and η_{sp}/c of 0.15–0.50 dL/g. Solution ^{13}C NMR in $CDCl_3$ confirmed cyclic structures for the repeat units and suggested exclusive six-membered ring formation with cis-dominated configurations (70–95%) of the recurring cyclohexane ring. Kinetic consideration of the temperature dependence of cis/trans ratios indicated that a lower activation energy for cis formation is responsible for the cis-dominated configuration despite a smaller collision frequency factor for cis than for trans formation. DSC thermograms showed high glass transition temperatures for both the methyl ester (239 °C) and ethyl ester (195 °C) derivatives. No evidence of crystallization was evident. The high glass transition temperatures apparently result from the high stereoregularity of the cyclic units and the inherent stiffening effect of the cyclic groups in the polymer backbones. UV curing of the diacrylate ethyl ester using a photoinitiator gave clear, rigid films which were soluble in methylene chloride. These new monomers and polymers incorporate functionality suitable for piezoelectric applications.

Introduction

We have been exploring the rich chemistry of the family of α-(hydroxymethyl)acrylates (1 in Figure 1) obtained from the inexpensive starting materials alkyl acrylates and paraformaldehyde.[1–3] The ether dimers (**2**) can be obtained in excellent yields without isolation of the α-(hydroxymethyl)acrylates and were found, under radical conditions, to give novel cyclopolymers containing tetrahydropyran units in the polymer backbone.[4–6] We also reported that α-(chloromethyl)acrylate (**3**) obtained by treating the α-(hydroxymethyl)acrylate with excess thionyl chloride can be converted to a variety of functional derivatives.[7,8]

As shown in an earlier study on cyclopolymerization of α,α′-dimethylenepimelates (**4**)[9–11] and in a more recent study on cyclopolymerization of **2**,[4,5,12,13] diacrylates having the general formula shown in Figure 2 are excellent cyclomonomers, giving high polymerization rates, high cyclization efficiencies, low polymerization shrinkages, and high thermal stabilities for the resulting cyclopolymer. Consideration of the polymerizability of monofunctional analogs of the cyclomonomers should provide an indication of the effect of the central X moiety on the reactivity of this type of cyclomonomer. For instance, the electronegativity of X should affect the polymerization rate and the molecular weight of the cyclopolymer while the bulkiness of X should have some steric affect on the cyclization efficiency and chain growth as suggested in a study of the cyclopolymerization of *N*-alkyldimethacrylamide.[14] For example, α-(hydroxymethyl)acrylates polymerize well while α-alkylacrylates other than the methacrylates do not polymerize at room temperature with radical initiators due to steric inhibition.

We decided to investigate incorporation of the malononitrile group as the connecting unit because of its strong electronegativity, relatively low steric bulkiness, and the ease of monomer synthesis through malonate alkylation chemistry. Another attractive feature of this approach is the potential for generating piezo- and pyroelectric properties in the resulting polymers owing to the large dipole moment of the dicyano group (similar to that reported for vinylidene cyanide copolymers).[15] We describe here the results to date on the synthesis, cyclopolymerization, and characterization of new dicyano-containing diacrylates derived from α-(chloromethyl)acrylates and malononitrile.

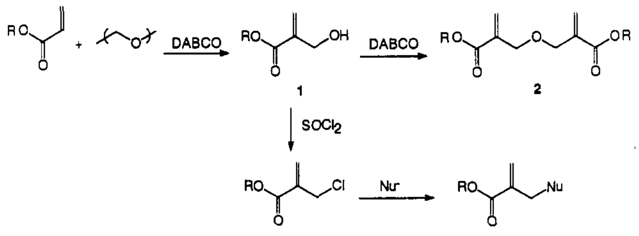
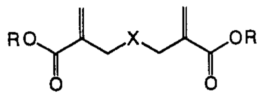


Figure 1. Synthesis of multifunctional acrylates via α-(hydroxymethyl)acrylates.



2 X = O
4 X = CH_2
5 X = $C(CN)_2$

Figure 2. General formula for cyclopolymerizable diacrylates.

Experimental Section

tert-Butyl α-(hydroxymethyl)acrylate (t-BHMA)[5] and ethyl α-(chloromethyl)acrylate (ECMA)[7] were prepared using previously published procedures. Malononitrile, tetrabutylammonium bromide (TBAB), and thionyl chloride were purchased from Aldrich Chemical Co. and used as obtained. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methyl alcohol before use. ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-300 spectrometer. Thermal transitions were measured on a Du Pont 9900 thermal analyzer using a Model 910 DSC cell at a heating rate of 10 °C/min under a nitrogen flow. Viscosity measurements for cyclopolymers were determined at 30 °C in acetone (for the methyl ester) or chloroform (for the ethyl ester) using a Cannon Ubbelohde #50 microviscometer.

Synthesis of Methyl α-(Chloromethyl)acrylate (MCMA). To a 100-mL one-neck round-bottom flask were added t-BHMA

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

0024-9297/93/2226-6359$04.00/0

Table I. Results of Cyclopolymerization of Dicyano-Containing Diacrylates

run no.[a]	[M][b] (mol/L)	[AIBN] (wt %)	temp (°C)	time (h)	conv (%)	f_c[c]	cis/trans[d] (%)	η_{sp}/c[e] (dL/g)	T_g[f] (°C)
M-1	4.35	1.3	94	1	64.0	0.994	83/17	0.15	233
M-2	4.35	0.2	70	20	56.1	0.997	91/9	0.17	239
E-1	0.83	1.0	80	3	30.0	ca. 1		0.11	182
E-2	2.17		80	0.3	4.1	ca. 1			
E-3	3.93	0.3	80	2	58.2	ca. 1	74/26	0.16	191
E-4	3.93	1.0	60	64	76.1	0.994	81/19	0.22	192
E-5	3.93	1.0	40	62	50.0	ca. 1	86/14	0.30	192
E-6	3.93	0.2	40	62	39.0	ca. 1	90/10	0.31	194
E-7	3.93		25	168	9.1	0.996	93/7	0.50	195

[a] M-1 and M2, methyl ester; E-1 to E-7, ethyl ester; E-2 and E-7 were polymerized without initiator. [b] Bulk polymerization except for E-1 and E-2 (solution polymerization in MEK). [c] Fraction of cyclized unit calculated from ^{1}H NMR spectra. [d] Calculated from ^{13}C NMR spectra. [e] Measured at 0.5 g/dL in acetone solution (methyl ester) or chloroform solution (ethyl ester). [f] Measured by DSC at 10 °C/min in a N_2 flow.

(46.9 g, 0.296 mol) and thionyl chloride (612 g, 5.14 mol), and the mixture was stirred at ambient temperature for 24 h. After the volatile components were evaporated, the residue was distilled to give α-(chloromethyl)acryloyl chloride (CMAC) in 74% yield. To a stirring mixture of methyl alcohol (6.96 g, 0.218 mol), triethylamine (22.0 g, 0.218 mol), and diethyl ether (100 mL) at a temperature below 10 °C was added slowly a mixture of CMAC (30 g, 0.217 mol) and diethyl ether (100 mL). The temperature was maintained below 10 °C for 12 h before keeping it at ambient temperature for another 12 h. The mixture was diluted with 100 mL of CH_2Cl_2 and extracted three times with 50 mL of water. The organic layer was separated and evaporated under reduced pressure to give crude MCMA in 70% yield. The crude MCMA was distilled under vacuum, mixed with *n*-hexane, and washed with 0.5 M KOH several times. After *n*-hexane was removed, 3.83 g of pure MCMA was obtained as a clear liquid (purity 98.2% by GC): ^{1}H NMR ($CDCl_3$) δ 6.37 (s, 1H), 5.99 (s, 1H), 4.29 (s, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.4, 137.0, 128.7, 52.2, 42.6.

Synthesis of Diacrylate 5a. To a stirring mixture of MCMA (3.2 g, 23.8 mmol), malononitrile (0.95 g, 14.4 mmol), TBAB (0.038 g, 0.118 mmol), and methylene chloride (12.0 g) was added a mixture of KOH (1.85 g, 28.6 mmol) in water (12.0 g). The mixture was stirred at ambient temperature for 2 h. The reaction conversion to diacrylate was estimated to be 91% by GC. The organic layer was separated, evaporated under reduced pressure, and distilled under vacuum. Pure diacrylate **5a** was obtained as a clear viscous liquid in 63% yield. Once crystallized at lower temperature, the crystals had a melting point of 63 °C: ^{1}H NMR ($CDCl_3$) δ 6.61 (s, 1H), 6.09 (s, 1H), 3.82 (s, 3H), 3.05 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 166.0, 132.6, 114.4, 52.6, 38.5, 37.8.

Synthesis of Diacrylate 5b. To a stirring mixture of ECMA (27.0 g, 0.183 mol), malononitrile (6.0 g, 0.091 mol), TBAB (0.58 g, 0.0018 mol), and methylene chloride (100 g) was added a mixture of KOH (11.74 g, 0.182 mol) and water (100 g). The mixture was stirred at ambient temperature for 1 h. The organic layer was separated and evaporated under reduced pressure to give 24.5 g of crude **5b** (yield 93%, purity 90% by GC). Repeated vacuum distillation gave the pure diacrylate **5b** as a clear viscous liquid in 48% yield: ^{1}H NMR ($CDCl_3$) δ 6.87 (s, 1H), 6.07 (s, 1H), 4.24 (q, 2H), 3.06 (s, 2H), 1.33 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 165.5, 133.0, 132.2, 114.5, 61.7, 38.3, 37.7, 14.1.

Typical Polymerization Conditions. Polymerizations were carried out by adding AIBN to 1 g of diacrylate in a small round-bottom flask equipped with a magnetic stirring bar. The mixture was subjected to nitrogen deaeration and then placed in an oil bath preheated to the temperature indicated in Table I. The resulting polymer was purified by reprecipitation into methyl alcohol twice. Two solution polymerizations were carried out for **5b** using methyl ethyl ketone as solvent; these are entries E-1 and E-2 in Table I. Polymerization conversions were determined from the product weight after the first precipitation. The fraction of cyclized units in the cyclopolymer was calculated from the intensity ratio of double-bond protons (6.0–6.7 ppm) to the methyl plus methylene protons (0.3–5.4 ppm) in the ^{1}H NMR spectra of the purified samples.

Results and Discussion

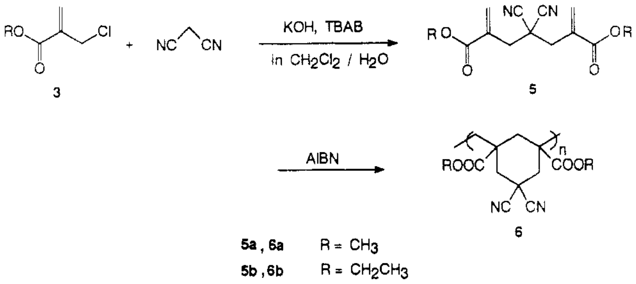


Figure 3. Synthesis and cyclopolymerization of dicyano-containing diacrylates.

The two ester derivatives of diacrylate **5** were synthesized as outlined in Figure 3. Using an equivalent or slight excess of malononitrile with methyl and ethyl α-(chloromethyl)acrylates in H_2O/CH_2Cl_2 at ambient temperature with a phase transfer catalyst and KOH was found to give almost quantitative yields of the dimers. The initial exotherm which caused the CH_2Cl_2 to reflux subsided in ca. 30 min. Easily identified byproducts such as various monofunctional acrylate derivatives were not detected by GC. Clearly, displacement of the chlorine of α-(chloromethyl)acrylate esters was fast and clean due to the occurrence of allylic attack as mentioned previously.[7] Both diacrylates were purified by distillation and identified by ^{1}H and ^{13}C NMR spectra (the latter are given in Figure 4). One interesting feature of the ^{13}C NMR spectra is the proximity of the two double-bond carbon peaks. Smaller chemical shift differences (<1 ppm) compared to those of the ether dimers (10–14 ppm) arise from the strong electron-withdrawing effect of the two cyano groups on the β-carbon to the vinyl groups and/or through space deshielding of the vinyl CH_2 groups. Such polarization might be expected to enhance polymerizability due to greater stabilization of the radical intermediates, although steric interactions by the two nitriles with approaching monomer may play an opposite role.

Table I shows the results of the cyclopolymerization study. Polymerziation of the diacrylates at 25–94 °C by AIBN proceeded smoothly without cross-linking even in neat monomer. As shown in Table I, the fractions of cyclized units f_c calculated from the relative intensity of vinyl methylenes in the ^{1}H NMR spectra were very close to 1 in all cases, confirming virtually complete cyclization. This was true for low- and high-conversion polymerization experiments. Such high cyclization efficiency is surprising because the corresponding ether dimer of the ethyl ester derivative, for example, gave an f_c value of 0.82 as determined from kinetic parameters obtained under the same conditions as for entry E-2. This efficient cyclization is attributed to the presence of the bulky cyano groups which would sterically repulse the two vinyl groups to give a conformation favorable for cyclization.[15] Another possible reason for efficient cyclization may be a low ceiling temperature for intermolecular monomer addition. That is, intermolecular addition before cyclization (resulting in

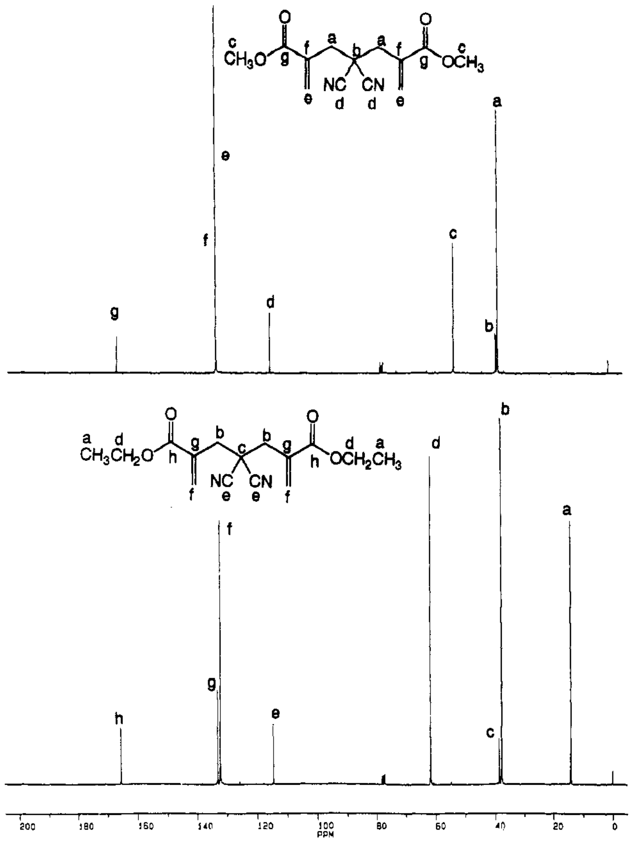


Figure 4. ^{13}C NMR spectra ($CDCl_3$) of dicyano-containing diacrylates: methyl ester (top trace); ethyl ester (bottom).

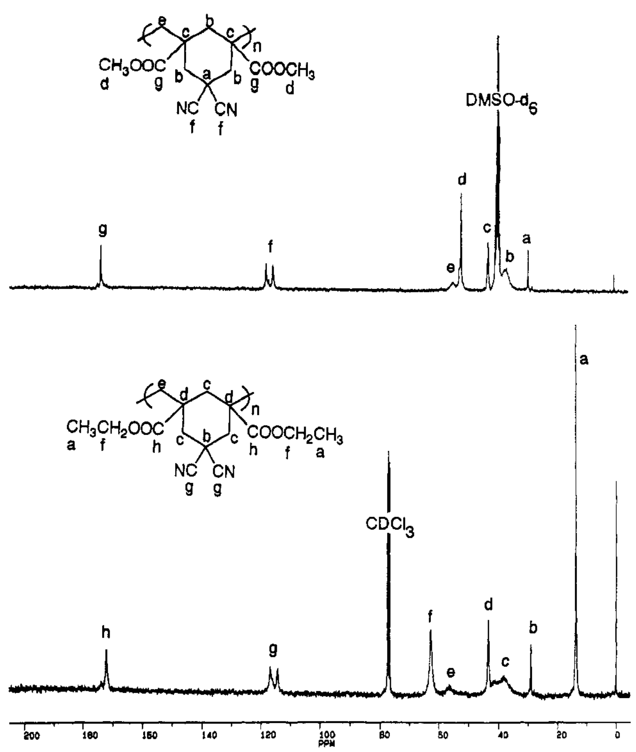


Figure 5. ^{13}C NMR spectra of cyclopolymers: methyl ester (top trace); ethyl ester (bottom).

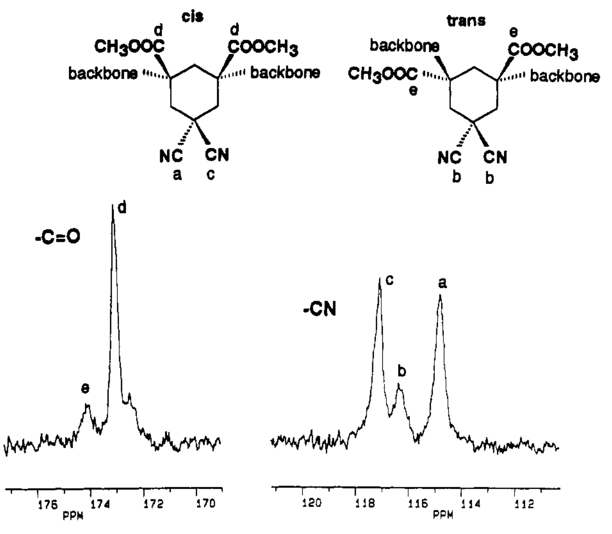


Figure 6. ^{13}C NMR spectrum of methyl ester cyclopolymer cyano region (right) and carbonyl region (left).

pendent unsaturation) may be inhibited by a low ceiling temperature for the acyclic linkage with the result that depolymerization occurs and cyclization is enhanced by default. On the other hand, the molecular weights of the cyclopolymers were relatively low compared with those from the corresponding ether dimers. A trace of impurities or the susceptibility of allyl protons in the diacrylates to chain transfer reaction might be responsible. Another possibility is the potential for the terminal radical formed to undergo radical cleavage such as that observed for thioether-containing acrylates.[16] An initial UV-initiated bulk polymerization evaluation with 2,2-dimethoxy-2-phenylacetophenone as photoinitiator at room temperature gave a clear rigid film within 10 min. This film was soluble in CH_2Cl_2, which again confirmed the high degree of cyclization without cross-linking.

Figure 5 shows the ^{13}C NMR spectra for the cyclopolymers. Structural assignments were made by referring to the spectra for the cyclopolymers derived from corresponding ether dimers, along with ^{13}C–^{1}H coupled experiments. Two sharp peaks seen at 29 and 43 ppm were found to be quaternary carbons. The smaller peak at 29 ppm was attributed to the carbon linked to two cyano groups with a ca. 9.5 ppm upfield shift (compared to monomer) caused in part by γ gauche interactions. The peak at 43 ppm is assigned to the backbone quaternary carbons; this is almost the same value as seen for the cyclopolymers of the ether dimers. Because only one set of peaks was observed for each quaternary carbon in the chemical shift range below 100 ppm, cyclopolymers obtained here are presumed to contain exclusively six-membered ring structures similar to those confirmed for the ether dimer polymers by ^{13}C nutation NMR spectroscopy.[6] Additionally, the peak assignments shown in Figure 5 are in good agreement with those of poly(dimethyl α,α'-dimethylenepimelate) (from monomer 4 in Figure 2).[17] The cyano carbons show multiple peaks at 114–118 ppm consisting of two major peaks and one minor peak. Figure 6 shows an expanded portion containing the cyano and carbonyl regions of the methyl ester polymer obtained at the highest temperature (94 °C) used in this study.

The assignments given in Figure 6 for the three cyano peaks for cis/trans isomers are consistent with both a necessary condition of a 1:1 intensity ratio for the two cis peaks and the chemical shift order expected from the shielding effect of the bulky polymer chain causing the "a" group to appear at higher field. The carbonyl region displays two peaks (beyond multiple peaks associated with tacticity between repeat units) that are assigned to trans and cis ring structures ("e" and "d", respectively). The ratio of peak intensities confirms cis-dominated configuration for the cyclopolymers. ^{1}H NMR spectra also suggested a high cis selectivity in which the ester methyl protons showed a strong peak (3.6 ppm) with a small shoulder (at 3.7 ppm) similar to the cis/trans splitting reported by Kim and co-workers.[17] The cis selectivity

Table II. Peak Intensity Ratio of Cyano and Carbonyl Regions of the ^{13}C NMR Spectrum of the Methyl Ester Cyclopolymer

temp (°C)	intensity ratio C═O e/d	intensity ratio CN c/b/a
70	11/89	45/9/46
94	17/83	42/17/41

observed is in contrast to the results of the cyclopolymerization of dimethyl α,α'-dimethylenepimelate by GTP (group transfer polymerization) which gave a complicated ^{13}C NMR spectrum owing to low stereoregularity. The ratios of trans to cis configurations calculated from the intensity ratios e/d and b/(a + c) in Table II are virtually identical. As clearly shown in Table II, the cis configuration increases as the polymerization temperature decreases.

The intermolecular propagating step detremining cis and trans configurations of the cyclohexane units involves monomer addition to the cyclized radical as shown in Figure 7. Based on Arrhenius equations, the ratio of rate constants of cis and trans addition is expressed by

$$\ln(k_{\mathrm{cis}}/k_{\mathrm{trans}}) = \ln(A_{\mathrm{cis}}/A_{\mathrm{trans}}) + (E_{\mathrm{trans}} - E_{\mathrm{cis}})/RT$$

With the ratios of cis and trans groups listed in Table I as $k_{\mathrm{cis}}/k_{\mathrm{trans}}$ in this equation, plots of $k_{\mathrm{cis}}/k_{\mathrm{trans}}$ versus the reciprocal of temperature gave straight lines for both the methyl and ethyl ester polymers as shown in Figure 8. The difference of activation energy $E_{\mathrm{trans}} - E_{\mathrm{cis}}$ was estimated to be 7.2 kcal/mol (methyl ester) and 6.0 kcal/mol (ethyl ester) from the slopes of the plots. The ratios of collision frequency factors $A_{\mathrm{trans}}/A_{\mathrm{cis}}$ were similarly estimated to be 3700 (methyl ester) and 1800 (ethyl ester) from the intercepts. Positive values of $E_{\mathrm{trans}} - E_{\mathrm{cis}}$ imply that cis formation dominates over trans formation energetically, while the large $A_{\mathrm{trans}}/A_{\mathrm{cis}}$ values mean that cis formation is disadvantageous sterically. Overall, it is concluded that the cis-dominated configuration observed for these diacrylates results from a stronger contribution from activation energy differences than steric factor effects. The unfavorable steric effect for cis formation is due to the presence of the bulky polymer chain on the same side of the ring as the incoming monomer (as shown in Figure 7). On the other hand, the reason for the activation energy advantage for cis formation (which overall controls stereoselectivity in these cyclopolymerizations) is not clear. It can be concluded, however, that the methyl ester monomer has a slightly higher cis selectivity than the ethyl ester compound over the temperature range of this study.

Figure 9 illustrates four possible microstructures for the cyclopolymers which correspond to four triads (mm, rm, mr, and rr) in polymethacrylates. As mentioned before, cis/trans isomerization caused a chemical shift difference of 1 ppm for carbonyl carbons in which the cis isomer was at higher field than the trans isomer (Figure 6). The studies on the microstructure of polymethacrylates published to date have shown that the meso diad peak occurs at higher field than the racemic peak for carbonyl carbons.[18,19] From the cis/trans isomer data for the cyclopolymers obtained here plus the meso/racemic data for several polymethacrylates published, it is reasonable to expect that the carbonyl carbon peaks of the meso isomers of the cyclopolymers also should appear at higher field. In fact, the cis carbonyl peak at 173.1 ppm in Figure 6 has a small shoulder on the high-field side. We believe that the main peak at 173.1 ppm corresonds to racemic-cis structures and the small peak at ca 172.5 ppm to meso-cis structures. The smaller chemical shift difference (0.6 ppm) compared with the cis/trans difference (1.0 ppm) is consistent with the results of poly(1,5-hexadiene) characterization which showed that cis/trans isomerization across the cyclopentane ring had a larger effect on the chemical shift differences than meso/racemic isomerization through the methylene bridge.[20] The peak intensity ratio of the presumed racemic-meso peaks for the cis isomer is estimated to be 80/20. Accordingly, the main structure among the four given in Figure 9 is concluded to be the racemic-cis structure, the fraction of which is calculated to be 72% for the cyclopolymer having 80% racemic and 90% cis structure and assuming the Bernoullian model ($P_{\mathrm{racemic}} \times P_{\mathrm{cis}} = 0.8 \times 0.9$). Similarly, the fraction of cis-syndiotactic diad shown in Figure 10 (which represents one of the more highly ordered structures for cyclopolymers[21]) is calculated to be ca. 65% ($P_{\mathrm{cis}} \times P_{\mathrm{racemic}} \times P_{\mathrm{cis}} = 0.9 \times 0.8 \times 0.9$). These numbers indicate unusually high stereoselectivity for this cyclopolymerization in spite of radical propagation. Further study might allow complete elucidation of the detailed microstructure of these cyclopolymers and the stereoregulation mechanism. Although we assumed a simple Bernoullian model for the above calculation, higher statistical models (such as the first-order Markov one) might be more appropriate

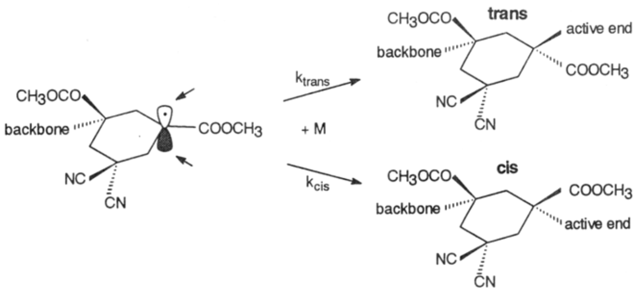


Figure 7. Possible addition mechanism resulting in cis and trans rings.

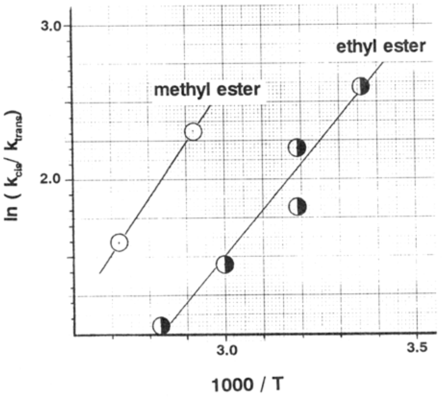


Figure 8. Relationship between $\ln(k_{\mathrm{cis}}/k_{\mathrm{trans}})$ and $1000/T$.

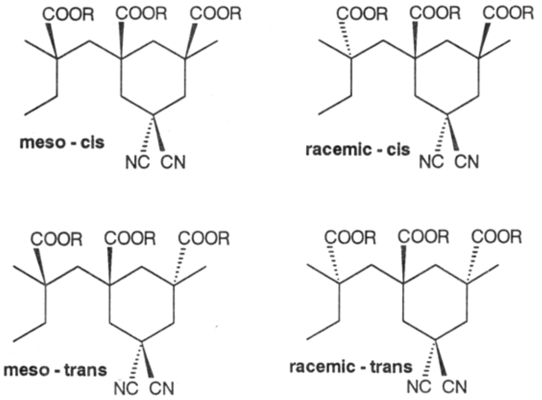


Figure 9. Possible microstructures of the cyclopolymers from dicyano-containing diacrylates.

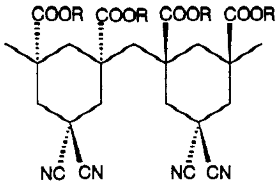


Figure 10. Cis-syndiotactic diad of the cyclopolymers (cis–racemic–cis).

for meso/racemic selection in this type of cyclopolymerization.

DSC analysis of the cyclopolymers showed unexpectedly high glass transition temperatures of 239 (methyl ester) and 195 °C (ethyl ester) (see Table I) compared with those from the corresponding ether dimers (methyl ester T_g of 165 °C,[4] ethyl ester 70–90 °C) and poly(α,α'-dimethylenepimelate) (methyl ester 111 °C).[17] In addition to the rigid and polar ring structure containing the malononitrile unit, the high stereoregularity described may be responsible for the large differences. The T_g of the cyclopolymers increased slightly with molecular weight as shown in Table I. No endotherm was observed in the thermograms, which suggests totally amorphous states for these polymers. Strong exotherms were seen with onset temperatures of ca. 290 (methyl ester) and 340 °C (ethyl ester), which are attributed to cyclization or related reactions between cyano groups. Such intramolecular reactions are characteristic of cyano-containing polymers and are used in the formation of carbon fibers from polyacrylonitrile. The high T_g's observed here might offer increased thermal stability of piezo- and pyroelectric properties that should be available with such materials by analogy with the behavior of poly(vinylidene cyanide) copolymers.[15]

Conclusions

New monomers have been synthesized and cyclopolymerized with almost complete cyclization efficiency to give novel polymers with novel properties. These dicyano-containing cyclopolymers have an unusual cis-dominated configuration in the repeat unit cyclohexane ring and showed unexpectedly high glass transition temperatures. Kinetic consideration of the temperature dependence of the cis/trans ratios indicated that lower activation energies for cis formation are responsible for the preferred cis configuration. The high T_g's observed are believed to arise from the high stereoregularity of the cyclopolymers coupled with incorporation of very polar malononitrile groups into the rigid cyclic structures in the polymer backbones.

Acknowledgment. This research was funded in part by Toagosei Chemical Industry Co. Ltd. and in part by the National Science Foundation through Grant DMR-9111903. T.T. wishes to thank the Mathias Research Group, especially Robert D. Thompson, for help and advice during this research.

References and Notes

(1) Mathias, L. J.; Kusefoglu, S. H.; Kress, A. O. *Macromolecules* **1987**, *20*, 2039.
(2) Mathias, L. J.; Kusefoglu, S. H.; Kress, A. O. *Macromolecules* **1987**, *20*, 2326.
(3) Colletti, R. F.; Halley, R. J.; Mathias, L. J. *Macromolecules* **1991**, *24*, 2043.
(4) Mathias, L. J.; Kusefoglu, S. H.; Ingram, J. E. *Macromolecules* **1988**, *21*, 545.
(5) Mathias, L. J.; Warren, R. M.; Huang, S. *Macromolecules* **1991**, *24*, 2036.
(6) Mathias, L. J.; Colletti, R. F.; Bielecki, A. *J. Am. Chem. Soc.* **1991**, *113*, 1550.
(7) Warren, S. C.; Mathias, L. J. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1637.
(8) Thompson, R. D.; Jarrett, W. L.; Mathias, L. J. *Macromolecules* **1992**, *25*, 6455.
(9) Marvel, C. S.; Vest, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5771.
(10) Marvel, C. S.; Vest, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 984.
(11) Milford, G. N. *J. Polym. Sci.* **1959**, *41*, 295.
(12) Tsuda, T.; Mathias, L. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 499.
(13) Stansbury, J. W. *Macromolecules* **1991**, *24*, 2029.
(14) Yamada, B.; Saya, T.; Otsu, T. *Makromol. Chem.* **1982**, *183*, 627.
(15) Miyata, S.; Yoshikawa, M.; Tasaka, S.; Ko, M. *Polym. J.* **1980**, *12*, 857.
(16) Meijs, G. F.; Rizzaldo, E.; Thang, S. H. *Macromolecules* **1988**, *21*, 3122.
(17) Kim, Y. B.; Choi, W. J.; Choi, B. S.; Choi, S. K. *Macromolecules* **1991**, *24*, 5006.
(18) Chujo, R.; Hatada, K.; Kitamaru, R.; Kitayama, T.; Sato, H.; Tanaka, Y. *Polym. J.* **1987**, *19*, 413.
(19) Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *24*, 4017.
(20) Cheng, H. N.; Khasat, N. P. *J. Appl. Polym. Sci.* **1988**, *35*, 825.
(21) Cavallo, L.; Guerra, G.; Corradini, P. *Macromolecules* **1993**, *26*, 260.