Competition between Diels-Alder Cycloaddition and Spontaneous Copolymerization of 1-Methoxy-1,3-butadiene with Electrophilic Olefins

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ABSTRACT: Concurrent Diels-Alder cycloaddition and spontaneous copolymerization occurred in the reactions of 1-methoxy-1,3-butadiene (MBD) with six electrophilic olefins at 25 °C. Reaction of fumaronitrile with MBD produced high molecular weight alternating copolymers and cycloadduct mixtures, even in dilute solutions. MBD reacted with maleic anhydride in bulk to produce mixtures of cycloadducts and low molecular weight alternating copolymers, while in solution only [4+2] cycloadducts were obtained. When the more electrophilic trisubstituted olefins trimethyl ethylenetricarboxylate, dimethyl cyanofumarate, and methyl β,β-dicyanoacrylate reacted with MBD, copolymerization competed with the concerted cycloaddition. Increasing electrophilicity of the olefin increased the yield of cycloadducts at the expense of that of copolymers. The less electrophilic acrylonitrile did not react with MBD at room temperature, while at 70 °C oligomers are formed. The proposed initiation mechanism in each case involves a 2-hexene-1,6-diyl diradical intermediate formed from the s-trans diene and the electrophilic olefin, which initiates the diene-olefin alternating copolymerization. The diene in the s-cis conformation cycloadds in concerted fashion to the electrophilic olefins, giving Diels-Alder adducts with retained stereochemistry.

Introduction

Recently, we have studied the spontaneous reactions of electron-rich alkyl and aryl 1,3-dienes and electrophilic olefins.[1-3] Although the expected Woodward-Hoffmann-allowed Diels-Alder cycloadditions were observed, reproducible spontaneous polymerizations accompanied these cycloadditions. Those studies extended our in-depth investigation of the spontaneous polymerizations which occur upon mixing an electron-rich olefin with an electron-poor olefin.[4-7] In the olefin-olefin systems the initiating species of the observed polymerizations was postulated to be the tetramethylene intermediates known to be formed in the accompanying stepwise [2+2] cycloadditions: bond formation occurs between the two olefins resulting in a zwitterionic or diradical tetramethylene intermediate depending on the substituents, which then initiates the observed ionic or free radical polymerizations, respectively. For the spontaneous polymerizations observed in the diene-olefin systems, we postulated a similar initiation mechanism in which a bond forms between the diene and the olefin resulting in a π-allyl 2-hexene-1,6-diyl diradical. This species was proposed to initiate the observed free radical copolymerizations.

In this study we extend our studies to 1-methoxy-1,3-butadiene (MBD), a conjugated diene which is more electron-rich than the alkyl and aryl dienes studied earlier. This diene is thermally stable under the reaction conditions used. It does not undergo deliberately initiated free radical homopolymerization but is able to copolymerize.[8-10] It is readily homopolymerized by cationic initiators such as trifluoroacetic or triflic acids.[8,11] The investigated electrophilic olefins are fumaronitrile (FN), maleic anhydride (MAnh), acrylonitrile (AN), and the trisubstituted electrophilic olefins trimethyl ethylenetricarboxylate (TrE), dimethyl cyanofumarate (DCF), and methyl β,β-dicyanoacrylate (MDA). All these olefins are stable in the reaction conditions. The trisubstituted electrophilic olefins do not homopolymerize spontaneously or even in the presence of free radical initiators[12] but readily undergo spontaneous free radical copolymerizations with electron-rich olefins. We will investigate the spontaneous thermal reactions of MBD with these electrophilic olefins and compare these results with the behavior of alkyl and aryl dienes. We will also comment on the work by Stepek,[10] who has previously studied the spontaneous polymerization of the MBD/Manh monomer pair.

Results

MBD was allowed to react with each of the investigated electrophilic olefins in 1:1 molar ratio at room temperature using different concentrations and solvents. The reactions were carried out under an argon atmosphere for 24 h in the absence of added initiator. From the resulting reaction mixtures, the polymeric fraction was precipitated and analyzed. The filtrate was analyzed to determine the yield and structure of any cycloadducts. Control experiments were run in the presence of a free radical initiator or inhibitor.

The highest copolymer yields were obtained in the reaction of MBD with FN. Table I shows the results obtained for this system in various solvents at different molar concentrations. Copolymerization dominates cycloaddition over the concentration range 3-5 mol/L, while at lower concentrations more cycloadduct is obtained. The expected [4+2] cycloadduct 4,5-dicyano-3-methoxy-1-cyclohexene was obtained as a yellow oily liquid. Only two isomers were observed as confirmed by GC and ^{1}H NMR analyses; the two cyano groups are always trans, in agreement with the concerted nature of the Diels-Alder cycloaddition. All the isolated copolymer samples possess high molecular weight (10^5) and alternating 1:1 structure, as proven by NMR and elemental analysis. As shown in Table I, the highest yield of copolymer was produced from $CHCl_3$ solutions, whereas the lowest copolymer yield was observed in acetonitrile. Table I also shows a remarkable increase of the copolymer yield upon raising the monomer concentration in all solvents. The polymerizations run in THF and acetonitrile stayed visually homogeneous, but

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Table I. Reactions of 1-Methoxy-1,3-butadiene with Fumaronitrile[a]

solvent	concn (M)	cycloadduct (% yield)	copolymer (% yield)	MW (SEC)
	bulk	16	79	
MeCN	5.0		74	
	4.0		68	
	3.0	49	52	
	2.0	61	43	
	1.0		28	
	0.5		12	
THF	5.0	0	95	
	4.0	0	92	
	3.0	16	83	
	2.0	43	46	
	1.0	66	20	
	0.5		5	
$CHCl_3$	3.0	10	96	1.7×10^6
	2.0	6	91	
	1.0	2	87	
$(CH_2Cl)_2$	4.0	12	84	2.7×10^5
	3.0	15	60	
	2.0	80	14	
	1.0	83	9	
CH_2Cl_2				
AIBN, 70 °C[b]	1.0	4	91	
MBE, UV[c]	1.0	6	95	
inhibitor[d]	3.0	94	0	

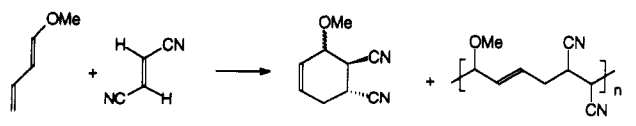
[a] Conditions: Reactions run at 1:1 molar ratio unnder an argon atmosphere for 24 h at 25 °C. Concentrations given are for each monomer. [b] AIBN (3 mol %) added; reaction run at 70 °C in CH_2Cl_2. [c] Benzoin methyl ether (2 mol %) added; reaction run under UV light at 25 °C in CH_2Cl_2. [d] Inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (3 mol %) added.

Table II. Reactions of 1-Methoxy-1,3-butadiene with Maleic Anhydride[a]

solvent	concn (M)	cycloadduct (% yield)	copolymer (% yield)	MW (SEC)
	bulk	82	11	450
MeCN	2.0	91	0	
dioxane	2.0	93	trace	
$(CH_2Cl)_2$	5.0	75	16	430
	3.0	94	0	
	2.0	96	0	
CH_2Cl_2	2.0	96	0	
AIBN, 70 °C[b]	1.0	42	32	450
BME, UV[c]	1.0	43	40	450
inhibitor[d]	5.0	96	0	

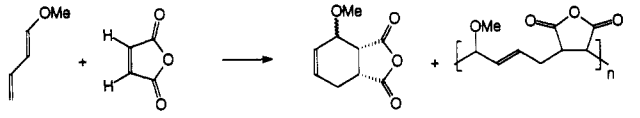
[a] Conditions: Reactions run at 1:1 molar ratio under an argon atmosphere for 24 h at 25 °C. Concentrations given are for each monomer. [b] AIBN (3 mol %) added; reaction run at 70 °C in CH_2Cl_2. [c] Benzoin methyl ether (2 mol %) added; reaction run under UV light at 25 °C in CH_2Cl_2. [d] Inhibitor (3 mol %) added.

the polymer precipitated out of the chlorinated solvents. Addition of very small amounts of free radical inhibitor prevented polymerization completely and 100% cycloadduct was produced. Higher yields of the same copolymer were obtained in the presence of deliberately added free radical initiator even at low monomer concentrations.



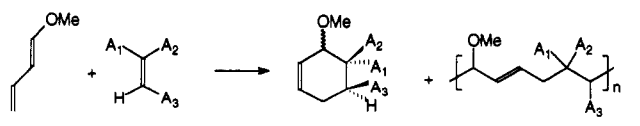
MBD FN

The MAnh–MBD reaction was studied in four different solvents at various concentrations and temperature. The obtained data are shown in Table II. For concentrations lower than 5 mol/L in each monomer, only the expected [4+2] cycloadduct was obtained as a mixture of two stereoisomers. In contrast to Stepek's results,[10] no copolymer was formed in dioxane if the solvent was scrupulously purified. Only at high concentration (5 mol/L) or in bulk experiments were both cycloadduct and oligomers produced. The copolymers possessed very low molecular weight (500) and alternating structure. Addition of free radical initiators greatly increased the copolymer yield, but the molecular weights did not increase. On the other hand, addition of an inhibitor completely stopped the copolymerization and only cycloadduct was obtained.



MBD MAnh

Reactions of TrE, the least electrophilic trisubstituted olefin,[13] with MBD were run in bulk and in dichloroethane solutions at 25 °C. As shown in Table III, the bulk experiment produced 50% copolymer. The copolymer yield decreased to 18% and 0% by lowering the monomer concentration to 3 and 2 mol/L, respectively. The alternating copolymers were of high molecular weight ($>10^5$) and film-forming. The cycloadduct was isolated as an oily liquid consisting of two isomers, as observed by NMR, namely, 3,5-*cis*- and 3,5-*trans*-4,4,5-tricarbomethoxy-3-methoxycyclohexene.



MBD TrE A_1, A_2, A_3 = COOMe
DCF A_1, A_3 = COOMe; A_2 = CN
MDA A_3 = COOMe; A_1, A_2 = CN

Table III. Reactions of 1-Methoxy-1,3-butadiene with Electrophilic Trisubstituted Olefins[a]

olefin	solvent	concn (M)	cycloadduct (% yield)	copolymer (% yield)	MW (SEC)
TrE		bulk	43	50	1.2×10^5
	$(CH_2Cl)_2$	3.0	78	18	1.6×10^5
		2.0	88	0	
	AIBN, 70 °C	2.0	52	42	
DCF		bulk	84	8	8.3×10^6
	MeCN	4.0	76	trace	
		3.0	68	trace	
	THF	4.0	72	trace	
		3.0	68	trace	
	$(CH_2Cl)_2$	4.0	88	6	5.8×10^6
		3.0	92	2	
		2.0	96	0	
	$CHCl_3$	4.0	93	0	
		3.0	95	0	
		2.0	96	0	
	CH_2Cl_2				
	AIBN, 70 °C[b]	2.0	65	16	6.2×10^6
	BME, UV[c]	2.0	66	18	
	inhibitor[d]	4.0	89	0	
MDA		bulk	87	7	2.1×10^4
	$(CH_2Cl)_2$	4.0	91	2	
		3.0	96	0	
	AIBN, 70 °C[b]	3.0	71	22	3.2×10^4

[a] Conditions: Reactions run at 1:1 molar ratio under an argon atmosphere for 24 h at 25 °C. Concentrations given are for each monomer. [b] AIBN (3 mol %) added; reaction run at 70 °C in CH_2Cl_2 for 5 h. [c] Benzoin methyl ether (2 mol %) added; reaction run under UV light at 25 °C in CH_2Cl_2. [d] Inhibitor (3 mol %) added.

Reaction of DCF with MBD was investigated in five solvents as shown in Table III. This reaction produced mainly [4+2] cycloadducts, as a mixture of only two isomers as shown by NMR. The two ester groups of DCF

Table IV. Comparison of Reactivities of Electrophilic Olefins

electrophilic character of olefin	olefin	LUMO[a] (eV)	CT color	reactivity rate in bulk	major product
lowest	TrE	−1.16	none	complete in 24 h	copolymer
↓	FN	−1.05	faint yellow	40 min (2.4 M)	↓
	MAnh	−1.62	yellow	10 min	
	DCF	−1.62	deeper yellow	fast	
highest	MDA	−1.72	deepest yellow	very fast	cycloadduct

[a] Calculated by AM1.[15]

remain trans to each other in the cycloadduct, in agreement with the concerted nature of the cycloaddition. In bulk and in highly concentrated dichloroethane solutions (>3 mol/L), small amounts of high molecular weight (10^6) alternating copolymers were separated. Deliberate free radical initiation, either at 60 °C or at 25 °C, resulted in only a 16% and 18% yield of copolymer, respectively, the remainder still being cycloadduct.

A similar situation was observed for the reaction of MDA and MBD, the most electrophilic of the investigated trisubstituted olefins.[13] A high yield of [4+2] cycloadduct was obtained, even in bulk. Both the 3,5-cis and 3,5-trans isomers of 5-carbomethoxy-4,4-dicyano-3-methoxycyclohexene were observed by NMR. A low yield of an alternating copolymer could be isolated at the highest monomer concentrations. Deliberate free radical initiation raised the copolymer yield to only 22%.

Acrylonitrile did not react with MBD at 25 °C, so it was investigated at 70 °C, at which temperature extensive reaction occurred. No cycloadduct was isolated. The product was mostly oligomeric (MW < 500) and displayed a prominent carbonyl absorption in the infrared spectrum (1724 cm^{-1}) and an aldehyde proton in the ^1H NMR spectrum at δ 9.5 ppm, which indicates substantial chain transfer. This is in contrast to the reported copolymerization of MBD with styrene, in which no chain transfer was observed.[14]

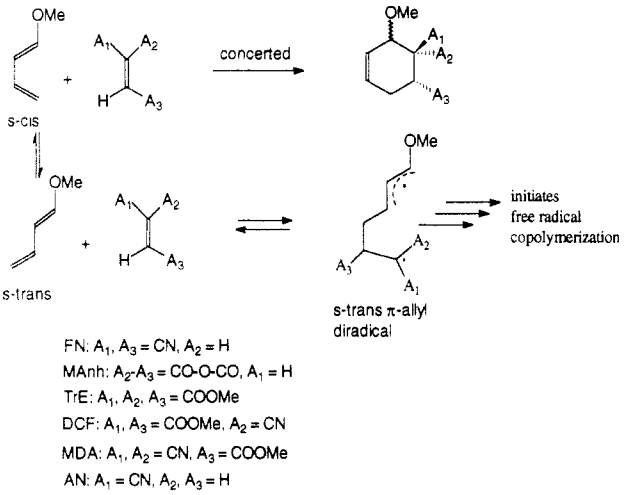
Charge transfer (CT) complexes were observed as colored solutions when all the monomer pairs were mixed. Their rate of fading served as a measure of the progress of the reactions. Attempts to observe the CT band by ultraviolet spectroscopy failed due to the rapid reactions which occur at the high concentrations necessary to observe the weak CT band. Reactions of the more active olefins could not be carried out in bulk in controlled fashion, because of exothermic reaction and viscosity buildup. The general trends are summarized schematically in Table IV.

The high molecular weight alternating copolymers obtained in this study all form clear, somewhat brittle, films and have T_g's in the range 88–118 °C. As far as copolymer solubility is concerned, the FN copolymer separated early in the polymerizations from the chlorinated solvents, mostly at the high concentrations. The polymerizing solutions at low concentrations stayed visually homogeneous but must be regarded as metastable, because these polymers cannot be redissolved in the same chlorinated solvents after precipitation, but they are still soluble in strong solvents. More polar solvents, such as THF and acetonitrile, gave homogeneous viscous polymerizing mixtures.

Discussion

The spontaneous reactions of 1-methoxybutadiene with electrophilic olefins occur readily, with the exception of the least reactive case, AN. Copolymers were obtained in most cases along with cycloadducts, even though no initiators or photoirradiation was used. The rates of reaction and the ratio of products were influenced by olefin structure, concentration, and solvent, not necessarily in

Scheme I



that order of importance. In the cases where cycloaddition predominated, deliberately added free radical initiators raised the copolymer yield. On the other hand, free radical inhibitors quenched copolymerization completely, while cycloaddition proceeded unchanged. In each case the cycloadduct was obtained as only two isomers, indicating preservation of olefin stereochemistry. Accordingly, the $_\pi4 + _\pi2$ cycloaddition is regarded as a classical Diels–Alder concerted reaction and the copolymerization as a classical free radical chain reaction. On the basis of our earlier work[6] and the fact that efficient copolymerizations are only observed for the least electrophilic comonomers, which form only weak CT complexes with MBD, we assume that the propagation proceeds by independent monomer addition, and not by homopolymerization of the CT complex.

The mechanism proposed to explain the observed reactions in this study (Scheme I) is analogous to the mechanism proposed for the reactions of alkyl and aryl dienes with electrophilic olefins. 1-Methoxybutadiene exists in both the s-cis and s-trans configurations. The s-cis form can undergo a concerted classical Diels–Alder reaction with the electrophilic olefin. The s-trans form can also react with the electrophilic olefin and form an s-trans π-allyl diradical. We postulate that this diradical can then initiate free radical chain copolymerization. Because the cycloadduct stereochemistry is that predicted by the concerted reaction, the cycloadduct does not form from this diradical intermediate.

Reactions were carried out at 25 °C for 24 h (except for AN). Even the less reactive olefins completely disappeared in this time to give copolymer, cycloadduct, and, in some cases, oligomer. In Table IV, the electrophilic olefins are listed in order of increasing electrophilicity. Additional cyano substituents increase the electrophilic character, as has been shown by cyclic voltammetry measurements.[13] Moreover, the LUMO levels of all these electrophilic olefins have been calculated by AM1[15] and are also included in Table IV.[16] A very good agreement is obtained between the observed reactivities in this study and the calculated LUMO levels, except for fumaronitrile. Olefin structure

played a major role in determining the cycloadduct/copolymer ratio: at the same concentrations the less electrophilic olefins gave more copolymer, and the more electrophilic olefins gave more cycloadduct.

The monomer concentration strongly influenced the product ratio. The yield of the FN copolymer increased remarkably between 1 and 3 M, and for TrE between 2 and 3 M. This concentration dependence of the cycloadduct/copolymer ratio is completely different from that for the reactions of alkyl-substituted dienes with AN, where a constant cycloadduct/copolymer ratio was found over a large concentration range.[2] The concentration dependence of copolymer formation in this work is too steep for a reasonable kinetics explanation. This leads us to believe that physical effects may be responsible for the odd concentration dependence observed in the MBD reactions. Anomalous kinetic behavior has previously been observed for cyano-containing polymers in poor solvents.[17]

If physical effects are influencing these reactions, then the solvent should also play a role in determining the cycloadduct/copolymer ratio in the product. Indeed, at the same concentrations, the chlorinated poor solvents gave less cycloadduct and more copolymer; the converse was true for the "good" solvents THF and MeCN, indicating that marginal solubility or insolubility increases the contribution of the copolymerization.

Finally, in contrast to Stepek's results,[10] no high yields of copolymer were obtained in the reaction of MBD with MAnh in dioxane. We conclude that his observations may have been due to peroxide contamination.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker WM-250 nuclear magnetic resonance spectrometer at 250 MHz. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are corrected. Gas chromatograms were obtained using a Varian 3300 GC with an OV-101 column. SEC data were obtained using THF as eluent, an ultraviolet detector, and a set of Phenomenex columns calibrated versus polystyrene standards. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Solvents. 1,2-Dichloroethane, methylene chloride, acetonitrile, and chloroform were dried over CaH_2 and distilled before use. Dioxane and THF were dried over sodium metal and distilled.

Reactants. 1-Methoxy-1,3-butadiene (99%, mixture of isomers) was received from Aldrich and used without further purification. Within the detection limits of the NMR only the *E*-isomer is present. Maleic anhydride (Aldrich) was distilled using a Kugelrohr distillation apparatus at 0.2 mmHg. Fumaronitrile (Aldrich) was recrystallized from methanol (mp 95–97 °C). The other trisubstituted electrophilic olefins were synthesized according to the reported procedures: dimethyl cyanofumarate,[6] methyl β,β-dicyanoacrylate,[18] and trimethyl ethylenetricarboxylate.[19]

Typical Reaction Procedure. The calculated amounts of MBD, electrophilic olefin, and solvent was transferred to a polymerization tube equipped with a vacuum valve. The reaction components were mixed at <−10 °C to avoid any sudden vigorous exothermic reaction. The solution was degassed using the freeze–thaw technique and kept under argon with stirring at the given temperature and reaction time. Then the reaction mixture was poured into a large excess of diethyl ether, containing a small amount of a free radical inhibitor. The precipitated polymeric materials were filtered, redissolved in acetone and reprecipitated in ether, thoroughly washed with warm ether, and dried under vacuum at 40 °C till constant weight. The obtained polymers were analyzed by IR, NMR, SEC, and elemental analysis. The filtrate was concentrated at room temperature using a rotary evaporator to isolate the produced cycloadducts. The cycloadducts were purified by washing several times with petroleum ether, dried under vacuum, and analyzed.

Control Polymerizations. 1-Methoxy-1,3-butadiene was heated at 70 °C for several days in the absence and in the presence of AIBN as a free radical initiator. Neither polymerization nor any other reaction was observed in either case. MBD undergoes efficient cationic homopolymerization in CH_2Cl_2 using triflic acid as an initiator at −70 °C. The dienophiles in this study do not undergo either spontaneous or deliberately initiated free radical homopolymerization, except for AN and to some extent MAnh.

Free radical copolymerizations, initiated by AIBN at 70 °C or by benzoin methyl ether (BME) with UV light (low-pressure mercury lamp) at 25 °C, of MBD with all the aforementioned olefins, except MAnh and AN, successfully produced a considerable yield of copolymer besides the expected [4+2] cycloadducts.

Physical Data of Cycloadducts and Copolymers. 4,5-Dicyano-3-methoxycyclohex-1-ene: Yellow oil which contains two isomers. IR (NaCl, cm^{-1}): 2247 (CN); 1655 (C=C). ^{1}H NMR ($CDCl_3$): δ 5.8 (2H, H_1, H_2, s); 4.1 (1H, H_3, m); 3.5 (3H, OCH_3, s); 3.0–3.2 (2H, H_4, H_5, m); 2.5–2.7 (2H, H_6, m). Anal. Calcd for $C_9H_{10}N_2O$: C, 66.58; H, 6.16; N, 17.26. Found: C, 66.25; H, 5.99; N, 17.09.

Copolymer of 1-methoxy-1,3-butadiene and fumaronitrile: T_g = 118 °C. IR (KBr, cm^{-1}): 2245 (CN); 1667 (C=C). ^{1}H NMR (acetone-d_6): δ 6.1, 5.7 (2H, vinyl H); 4.0 (1H, CHOMe); 3.6 (2H, CHCN); 3.4 (3H, OCH_3); 2.7 (2H, CH_2). Anal. Calcd for repeat unit $C_9H_{10}N_2O$: C, 66.58; H, 6.16; N, 17.26. Found: C, 65.82; H, 5.95; N, 17.07.

3-Methoxy-1,2,3,6-tetrahydrophthalic anhydride: mp 94–96 °C. IR (KBr, cm^{-1}): 1854, 1833, 1780 (anhydride); 1650 (C=C); ^{1}H NMR ($CDCl_3$): δ 6.1 (2H, H_1, H_2, t); 4.2 (1H, H_3, m); 3.16–3.22 (1H, H_4, m); 3.27–3.35 (1H, H_5, m); 3.26 (3H, OCH_3, s); 2.5–2.6 (2H, H_6, m). Anal. Calcd for $C_9H_{10}O_4$: C, 59.28; H, 5.49. Found: C, 59.38; H, 5.41.

Copolymer of 1-methoxy-1,3-butadiene and maleic anhydride: T_g = 123 °C. IR (KBr, cm^{-1}) 1860, 1782 (anhydride); 1650 (C=C). ^{1}H NMR (acetone-d_6): δ 5.8–6.0 (2H, vinyl H); 4.2 (1H, $CHOCH_3$); 3.4 (2H, anhydride H); 3.3 (3H, OCH_3); 2.7 (2H, CH_2). Anal. Calcd for repeat unit $C_9H_{10}O_4$: C, 59.28; H, 5.49. Found: C, 59.43; H, 5.40.

4-Cyano-4,5-bis(dimethoxycarbonyl)-3-methoxycyclohex-1-ene: Mixture of two isomers, mp 67–75 °C. IR (KBr, cm^{-1}): 2247 (CN); 1758, 1733 (C=O); 1652 (C=C). ^{1}H NMR ($CDCl_3$): δ 5.9–6.1 (2H, H_1, H_2, m); 4.25, 4.17 (1H, H_3, m, two isomers); 3.75, 3.9 (6H, $COOCH_3$, 2s); 3.4 (3H, OCH_3, s); 3.3 (1H, H_5, t); 2.1–2.4 (2H, H_6, m). Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.92; H, 5.92; N, 5.52. Found: C, 57.05; H, 5.89; N, 5.38.

Copolymer of 1-methoxy-1,3-butadiene and dimethyl cyanofumarate: T_g = 93 °C. IR (KBr, cm^{-1}): 2247 (CN); 1742 (C=O); 1652 (C=C). ^{1}H NMR ($CDCl_3$): δ 5.2 (2H, vinyl H, very broad); 4.0 (1H, CHOMe, broad); 3.7 (6H, $COOCH_3$, s); 3.2 (3H, OCH_3, s); 3.1 (1H, CHCOOMe, very broad); 2.6 (2H, CH_2, very broad). Anal. Calcd for repeat unit $C_{12}H_{15}NO_5$: C, 56.91; H, 5.92; N, 5.52. Found: C, 57.26; H, 5.89; N, 5.88.

4,4-Dicyano-5-(methoxycarbonyl)-3-methoxycyclohex-1-ene: Mixture of two isomers, mp 71–85 °C. IR (KBr, cm^{-1}): 2255 (CN); 1744 (C=O); 1650 (C=C). ^{1}H NMR ($CDCl_3$): δ 5.75, 5.95 (2H, H_1, H_2, m); 4.25 (1H, CHOMe, m); 3.86 (3H, $COOCH_3$, s); 3.68 (3H, OCH_3, s); 3.15 (1H, H_5, m); 2.5–2.6 (2H, H_6, m). Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 60.00; H, 5.4; N, 12.7. Found: C, 60.02; H, 5.37; N, 12.64.

Copolymer of 1-methoxy-1,3-butadiene and methyl β,β-dicyanoacrylate: T_g = 91 °C. ^{1}H NMR ($CDCl_3$): δ 5.9–6.0 (2H, vinyl H, broad); 4.3 (1H, CHOMe, broad); 3.85 (3H, $COOCH_3$); 3.65 (3H, OCH_3); 3.15 (1H, CHCOOMe); 2.6 (2H, CH_2). Anal. Calcd for repeat unit $C_{11}H_{12}N_2O_3$: C, 60.0; H, 5.4; N, 12.7. Found: C, 59.32; H, 5.32; N, 12.13.

4,4,5-Tris(methoxycarbonyl)-3-methoxycyclohex-1-ene: Mixture of two isomers. ^{1}H NMR ($CDCl_3$): δ 5.7–6.0 (2H, H_1, H_2, m); 4.35, 4.17 (1H, H_3, two isomers); 3.85–3.65 (6s, 3H each, $COOCH_3$); 3.5–3.3 (2s, 3H each, OCH_3); 3.25 (1H, H_5, m); 2.4 (2H, H_6, m). Anal. Calcd for building unit $C_{13}H_{18}O_7$: C, 54.5: H, 6.3. Found: C, 54.3; H, 6.15.

Copolymer of 1-methoxy-1,3-butadiene and trimethyl ethylenetricarboxylate: T_g = 88 °C. ^{1}H NMR ($CDCl_3$): δ 5.75,

5.25 (2H, vinyl H); 3.95 (1H, C*H*OMe); 3.68 (12H, COOCH_3, OCH_3, very broad); 3.1 (1H, C*H*COOMe); 2.6 (2H, CH_2). Anal. Calcd for repeat unit $C_{13}H_{18}O_7$: C, 54.5; H, 6.3. Found: C, 54.3; H, 6.15.

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