Competition between Cycloaddition and Spontaneous Copolymerization of 4-Methyl-1,3-pentadiene with Electrophilic Olefins

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ABSTRACT: Competition between cycloadditions and spontaneous copolymerizations in the reactions of 4-methyl-1,3-pentadiene (MPD; 1,1-dimethylbutadiene) with seven electrophilic olefins was investigated at two temperatures (25 and 70 °C) and in two solvents of different polarities (acetonitrile and 1,2-dichloroethane). Tetracyanoethylene (TCNE), the most electrophilic olefin, reacted with MPD to produce a mixture of [2 + 2] and [4 + 2] cycloadducts, and the ratio of these isomers depended mainly on solvent polarity. No polymerization was observed in this system. Both methyl β,β-dicyanoacrylate (MDA) and dimethyl cyanofumarate (DCF) reacted with MPD to produce mixtures of [4 + 2] and [2 + 2] cycloadducts and alternating copolymers. Reactions with fumaronitrile (FN), maleic anhydride (MAnh), and acrylonitrile (AN) with MPD produced only alternating copolymers and no cycloadducts. Trimethyl ethylenetricarboxylate (TrE), the least electrophilic investigated olefin, did not react at all with MPD even at 70 °C. All the obtained copolymers are of high molecular weight (10^4–10^5). The suggested mechanism involves the formation of a 2-hexene 1,6-diradical formed by reaction of the s-trans diene with the electrophilic olefin, which initiates the diene–olefin alternating copolymerization. This polar diradical is also the proposed intermediate in the [2 + 2] cycloaddition reaction. The diene in its s-cis conformation undergoes concerted Diels–Alder cycloaddition with the electrophilic olefins.

Introduction

In our earlier studies of the spontaneous reactions which occur upon mixing an electron-rich olefin with an electron-poor olefin, we found competing cycloaddition and polymerization reactions.[1–4] The initiating species for the observed polymerization was postulated to be the tetramethylene intermediate known to be formed in the [2 + 2] cycloadditions: bond formation occurs between the two olefins, resulting in a zwitterionic or diradial tetramethylene intermediate, which then initiates the ionic or free-radical polymerization, respectively. Similarly we have found that spontaneous reactions of electron-rich alkyl- and aryl-1,3-dienes with electrophilic olefins result in competing polymerization and cycloaddition reactions.[5–7] In these cases a π-allyl-2-hexene 1,6-diradical intermediate was postulated to be the initiator of the observed free-radical copolymerizations. Most recently we investigated the spontaneous thermal reactions of electrophilic olefins with 1-methoxy-1,3-butadiene,[8] a conjugated diene which is more electron-rich than the earlier studied alkyl- and aryl-1,3-dienes. Once again alternating copolymers were obtained alongside cycloadducts. The suggested mechanism is analogous to that proposed in the cases of the previously investigated diene/olefin systems.

In this paper we extend these studies to 4-methyl-1,3-pentadiene (MPD; 1,1-dimethylbutadiene), a conjugated diene whose nucleophilicity might be comparable with that of 1-methoxy-1,3-butadiene. However, its molecular structure, namely, the two methyl groups on the terminal carbon, might decrease the contribution of the [4 + 2] concerted Diels–Alder reactions with electrophilic olefins in favor of the copolymerization and/or [2 + 2] cycloaddition. MPD is thermally stable under the used reaction conditions. It does not undergo free-radical homopolymerization, but it is readily homopolymerized by a cationic mechanism.[9,10] Concerning its copolymerization a very limited number of reports was found in the literature.[11,12]

The investigated electrophilic olefins, in order of decreasing electrophilicity,[8] are tetracyanoethylene (TCNE), methyl β,β-dicyanoacrylate (MDA), dimethyl cyanofumarate (DCF), trimethyl ethylenetricarboxylate (TrE), fumaronitrile (FN), maleic anhydride (MAnh), and acrylonitrile (AN). All these olefins are stable in the reaction conditions. With the exception of AN, they do not homopolymerize spontaneously or even in the presence of free-radical initiators,[13] but MDA, DCF, and TrE copolymerize spontaneously with electron-rich olefins.[12] All electrophilic olefins in this study, except TCNE, copolymerize with electron-rich olefins in the presence of free-radical initiators.

Results

MPD was allowed to react with each of the investigated electrophilic olefins in a 1:1 molar ratio at two temperatures (25 and 70 °C), using different concentrations and two solvents of different polarities. From the product mixture, the polymeric fraction was precipitated in ether, purified, and analyzed. The filtrate was concentrated and analyzed to determine the yield and structure of the formed cycloadducts.

The reaction of TCNE, the most electrophilic olefin, with MPD did not yield any copolymer, but it produced a mixture of two cycloadducts. ^{1}H-NMR analysis showed that in acetonitrile the cycloadduct is 100% [2 + 2], 3-(2-methylpropenyl)-1,1,2,2-tetracyanocyclobutane, while in 1,2-dichloroethane a mixture of 60% of the cyclobutane derivative and 40% of the [4 + 2] cycloadduct, 3,3-dimethyl-4,4,5,5-tetracyanocyclohex-1-ene, was produced. These results are in perfect agreement with those previously reported by Stewart.[14]

Highest yields of both copolymer and cycloadducts were obtained from the methyl β,β-dicyanoacrylate (MDA)/MPD system. Table I shows the data for this reaction. In

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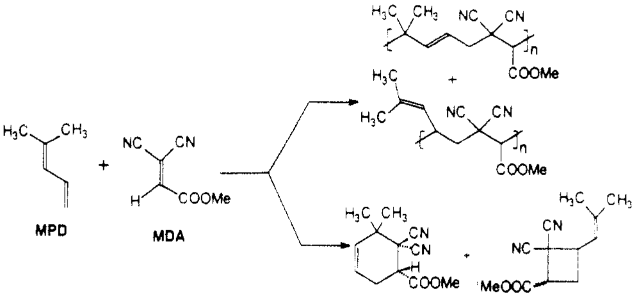
Table I. Reactions of 4-Methyl-1,3-pentadiene with Methyl β,β-Dicyanoacrylate (MDA) in a 1:1 Molar Ratio[a]

solvent	temp (°C)	conc (M)	time (h)	cycloadd (%)	copoly (%)	MW (SEC)
	25	bulk	24[d]	20	51	10^4
	70	bulk	24[d]	44	42	
CH$_3$CN	25	3.0	1	2	zero	
			16	50	48	2×10^4
		0.5	16	63	38	
	70	3.0	1	12	31	
			16	35	65	1.5×10^4
		0.5	16	54	45	
(CH$_2$Cl)$_2$	25	0.5	16	53	44	
	70	0.5	16	50	47	1×10^4
CH$_3$CN AIBN[b]	70	0.5	16	18	80	
inhibitor[c]	70	0.5	16	76	zero	

[a] Concentrations given are for each monomer. [b] AIBN (3 mol %) is added. [c] Inhibitor 2,2,6,6-tetramethylpiperidinoxy free radical; 3 mol % is added. [d] Reaction mixture solidified after 1–2 h.

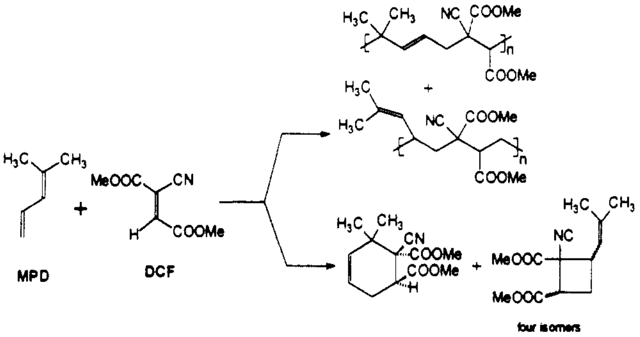


acetonitrile at room temperature more cycloadducts were produced than copolymer. The reaction reaches almost 100% conversion after 16 h, even at low concentration (0.5 M). Raising the temperature to 70 °C increases the copolymer to cycloadduct ratio. ^{1}H-NMR analysis shows that the copolymer obtained consists of a mixture of 1,4- and 1,2-addition products, with the 1,4-product dominating (75–86%) in all cases. All the isolated copolymers are alternating with high molecular weight (10^4). The cycloadducts produced in this reaction were a mixture of the [4 + 2] cycloadduct 4,4-dicyano-5-(methoxycarbonyl)-3,3-dimethylcyclohex-1-ene and the [2 + 2] cycloadduct 2,2-dicyano-1-(methoxycarbonyl)-3-(2-methylpropenyl)-cyclobutane. The cyclohexene derivative was always obtained as only one stereoisomer in agreement with the concerted nature of the [4 + 2] Diels–Alder reaction. The cyclobutane was obtained as two isomers, 1,3-cis and -trans. The ratio of cyclohexene to cyclobutane derivatives was always between 70 and 90%. Changing the solvent from acetonitrile to the less polar 1,2-dichloroethane slightly increased the copolymer yield and also increased the amount of cyclohexene derivative relative to cyclobutane. Addition of 3 mol % of free-radical inhibitor completely prevented the polymerization, while using a free-radical initiator markedly raised the copolymer yield.

Table II. Reactions of 4-Methyl-1,3-pentadiene with Dimethyl Cyanofumarate (DCF) in a 1:1 Molar Ratio[a]

solvent	temp (°C)	conc (M)	time (h)	cycloadd (%)	copoly (%)	MW (SEC)
	24	bulk	24[d]	15	50	6×10^4
	70	bulk	24[d]	30	55	5×10^4
CH$_3$CN	25	3.0	20	4	6	500
			50	6	7	520
			70	10	12	510
		0.5	70	trace	zero	
	70	3.0	20	10	27	470
					14	6.5×10^4
			70	20	30	470
					18	6×10^4
		0.5	20	1	3	450
					35	6×10^4
			70	4	6	460
					36	6×10^4
(CH$_2$Cl)$_2$	25	3.0	24	5	6	500
	70	3.0	24	12	20	510
					11	5×10^4
CH$_3$CN	70	3.0	24	4	32	500
					45	6×10^4
inhibitor[c]	70	3.0	24	9	zero	

[a] Concentrations given are for each monomer. [b] AIBN (3 mol %) is added. [c] Inhibitor 2,2,6,6-tetramethylpiperidinooxy; free radical, 3 mol % is added. [d] Reaction mixture solidified after 1–2 h.



The obtained data for the dimethyl cyanofumarate (DCF) reaction with MPD are summarized in Table II. Again this reaction was studied in two different solvents at two concentrations at two different temperatures. These reactions were much slower than the ones described above for MDA and MPD. Even after 70 h at 70 °C, the 3 mol/L solution only resulted in 46% conversion. Under all the investigated conditions the copolymer yield was always higher than that of the cycloadduct. At room temperature the copolymers obtained were just oligomers of about 500 molecular weight. Raising the temperature increased the total conversion (copolymer and cycloadducts) and produced a high molecular weight copolymer fraction (10^4) together with the oligomers. ^{1}H-NMR analysis revealed that both the oligomers and high molecular weight copolymers consisted of a mixture of 1,4- and 1,2-addition products. Again the 1,4-addition was found to be dominant (70–85%). The amount of formed oligomers was higher in concentrated solution (3 mol/L) than at 0.5 mol/L. The cycloadducts found in the filtrate were analyzed by NMR. It showed the presence of [4 + 2] cycloadduct dimethyl 4-cyano-3,3-dimethylcyclohex-1-ene-4,5-dicarboxylate (one stereoisomer) and [2 + 2] cycloadduct dimethyl 2-cyano-3-(2-methylpropenyl)cyclobutane-1,2-dicarboxylate (four stereoisomers). The cyclohexene percentage was between 68 and 90%. Using 1,2-dichloroethane as solvent had little effect on the yields and the product ratios.

For the reactions of FN, MAnh, and AN with MPD, the products were found to be exclusively high molecular weight copolymers under all the investigated reaction conditions. No cycloadducts were produced in these

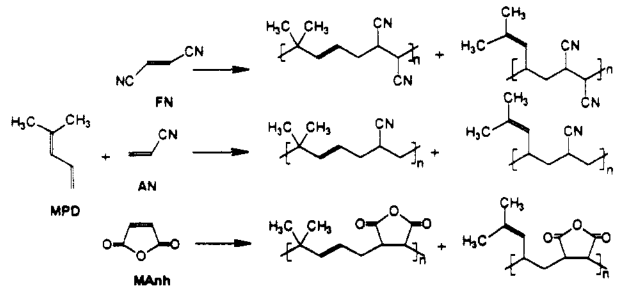


Table III. Reactions of 4-Methyl-1,3-pentadiene with Fumaronitrile (FN) in a 1:1 Molar Ratio[a]

solvent	temp (°C)	conc (M)	time (h)	copolym (%)	MW (SEC)
	25	bulk	24	zero	
	70	bulk	24[d]	76	1.5×10^4
CH_3CN	25	3.0	24	zero	
			50	10	2.1×10^4
			75	21	
			140	32	
		1.0	75	zero	
	70	3.0	24	86	2.7×10^4
		1.0	24	48	
			50	59	
			75	80	
			140	93	
		0.5	24	38	
$(CH_2Cl)_2$	70	3.0	24	89	2.5×10^4
		1.0	24	49	
CH_3CN					
AIBN[b]	70	3.0	24	99	
inhibitor[c]	70	3.0	24	zero	

[a] Concentrations given are for each monomer. [b] AIBN (3 mol %) is added. [c] Inhibitor 2,2,6,6-tetramethyl piperidinooxy free radical; 3 mol % is added. [d] Reaction mixture solidified after 1–2 h.

Table IV. Reactions of 4-Methyl-1,3-pentadiene with Maleic Anhydride (MAnh) in a 1:1 Molar Ratio[a]

solvent	temp (°C)	conc (M)	time (h)	copolym (%)	MW (SEC)
	25	bulk	24[d]	45	
	70	bulk	24[d]	100	1×10^5
CH_3CN	25	3	120	zero	
	70	4	24	95	1.5×10^5
		1	24	70	
			96	96	
$(CH_2Cl)_2$	25	3	120	zero	1×10^5
	70	4	24	96	
CH_3CN					
AIBN[b]	70	1	24	99	
inhibitor[c]	70	3	24	zero	

[a] Concentrations given are for each monomer. [b] AIBN (3 mol %) is added. [c] Inhibitor 2,2,6,6-tetramethylpiperidinooxy free radical; 3 mol % is added. [d] Reaction mixture solidified after 1–2 h.

systems. Table III contains the results of the FN–MPD reactions. At room temperature the reaction is very slow, even in bulk. No product was detected up to 24 h at 3 mol/L initial concentrations. After 50 h, 10% high molecular weight copolymer was produced. At 70 °C the reaction rate increased substantially. According to the NMR analysis the copolymers obtained consisted of a 1,4 and 1,2 mixture. Using 1,2-dichloroethane slightly increased the amount of copolymer formed. Addition of free-radical inhibitor completely prevented the copolymerization, while in presence of AIBN the reaction proceeded to 100% copolymerization.

Table IV shows the data of the MAnh–MPD reactions. In this case no reaction took place at room temperature, except in bulk. At 70 °C and 4 mol/L, a 95% yield of high molecular weight (10^5) copolymer was obtained after 24 h. At lower initial concentrations the rates were somewhat slower, but near-quantitative yields of copolymers were still obtained. Similar results were found in 1,2-dichloroethane. The acrylonitrile–MPD reactions led to similar results as MAnh, and they are summarized in Table V.

TrE, the least electrophilic investigated olefin, did not react with MPD even in bulk at 70 °C for 120 h. Crystals of TrE were recovered at the end of the reaction time.

All the high molecular weight copolymers obtained in this study form clear, somewhat brittle, films and have T_g's in the range of 110–135 °C.

Table V. Reactions of 4-Methyl-1,3-pentadiene with Acrylonitrile (AN) in a 1:1 Molar Ratio[a]

solvent	temp (°C)	conc (M)	time (h)	copolym (%)	MW (SEC)
	25	bulk	96	trace	
	70	bulk	96	95	6.3×10^4
CH_3CN	25	4	96	zero	
	70	2	24	55	6×10^4
			48	81	
			72	96	
		4	24	77	
$(CH_2Cl)_2$	70	4	24	83	
			72	91	6.2×10^4
CH_3CN					
AIBN[b]	70	2	24	88	
inhibitor[c]	70	4	72	zero	

[a] Concentrations given are for each monomer. [b] AIBN (3 mol %) is added. [c] Inhibitor 2,2,6,6-tetramethylpiperidinoxy free radical; 3 mol% is added.

Discussion

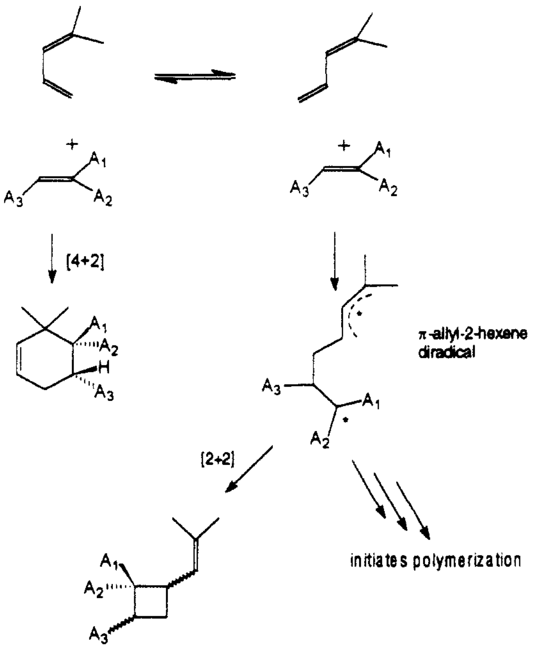
The reactivity of 4-methyl-1,3-pentadiene in spontaneous reactions with various electrophilic olefins is mainly influenced by the electrophilicity of the latter. TCNE, the most electrophilic olefin, in its reactions with MPD led only to cycloadducts, a mixture of [4 + 2] and [2 + 2]. MDA, next to TCNE in electrophilicity, reacted with MPD at room temperature to produce a mixture of alternating copolymer and cycloadducts. The cycloadduct still predominated and mainly consisted of the [4 + 2] Diels–Alder product. Raising the temperature increased the ratio of copolymer to cycloadduct. DCF, less electrophilic and more bulky than MDA, reacted with MPD to give a higher ratio of copolymer to cycloadduct, but in very low yields overall. Again high temperature favors the copolymerization reaction. All other less electrophilic investigated olefins (FN, MAnh, and AN) produced only copolymers, except for TrE which did not react at all. MAnh and AN copolymerized with MPD at high temperature only. All these copolymerization reactions are regarded as a radical chain reaction and can be completely quenched by a small amount of free-radical inhibitor or accelerated by a free-radical initiator.

Initial concentrations have an effect on the reaction rates and product ratio. Higher concentrations result in faster reactions and also favor copolymerization. In the case of DCF increasing the concentration led to increased oligomer formation. This could be a result of transfer reactions due to the bulky size of the ester substituents. The lower electrophilicity of DCF compared to TCNE and MDA results in a very small contribution of the cycloaddition.

Solvent polarity has a limited effect on all of these reactions in agreement with the radical nature of the intermediates. The only exception is the reaction of TCNE with MPD. Only cycloadduct is obtained in this case. The [4 + 2] cycloaddition is proposed to be concerted and therefore rather insensitive to solvent polarity. The competing [2 + 2] cycloaddition is stepwise and proceeds via a polar intermediate. Therefore, polar solvents favor the [2 + 2] cycloaddition. These TCNE results are in total agreement with literature data.[14]

In the MDA and DCF systems, the [4 + 2] cycloadducts were obtained as only one isomer, indicating preservation of olefin stereochemistry. This is in agreement with the concerted nature of these Diels–Alder cycloadditions. The [2 + 2] cycloadducts were obtained as two isomers in the case of MDA and four isomers for the DCF system. The former is a result of the two possible ways in which the two reactants can approach each other, the four isomers in the

Scheme I



• represents polar radicals

latter case reflect the stepwise mechanism of the [2 + 2] cycloaddition, allowing isomerization in the intermediate.

Scheme I shows the three proposed concurrent pathways leading to the formation of copolymers and [4 + 2] and [2 + 2] cycloadducts. MPD exists in both the s-cis and s-trans conformation. The s-cis form is ready to undergo a concerted classical Diels–Alder cycloaddition with strong electrophilic olefins. On the other hand, the s-trans form can react with electrophilic olefins to form a s-trans π-allyl-2-hexane 1,6-diradical which can then initiate free-radical chain copolymerization or cyclize to form the [2 + 2] cycloadduct.

A very good agreement is obtained between the observed olefin reactivity and their calculated LUMO levels.[8] The most electrophilic olefins have the highest cycloadduct/copolymer ratio. With the less electrophilic olefins only copolymers are obtained. This is the same trend as we have observed previously for 1-methoxybutadiene. The greater tendency of MPD to form [2 + 2] cycloadducts is due to the steric hindrance by the two terminal methyl groups which make the concerted [4 + 2] cycloaddition more difficult.

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 and acetonitrile were dried over CaH_2 and distilled before use. THF was dried over sodium metal and distilled.

Reactants. 4-Methyl-1,3-pentadiene was separated from its mixture with *trans*-2-methyl-1,3-pentadiene, 75% (Aldrich) according to the Bachman[15] method. Maleic anhydride (Aldrich) was distilled using a Kugelrohr distillation apparatus at 0.2 mmHg. Fumaronitrile and tetracyanoethylene (Aldrich) were recrystallized from methanol. The other trisubstituted electrophilic olefins were synthesized according to the reported procedures: dimethyl cyanofumarate,[6] methyl β,β-dicyanoacrylate,[16] and trimethyl ethylenetricarboxylate.[17] Acrylonitrile (Aldrich, bp 77 °C) was distilled just before use.

Typical Reaction Procedures. The calculated amounts of MPD, electrophilic olefin, and solvent were 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 to 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. 4-Methyl-1,3-pentadiene was heated at 70 °C for several days in the absence or presence of AIBN as a free-radical initiator. Neither polymerization nor any other reaction was observed in either case. MPD 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 methyl benzoin ether (MBE) with UV light (low pressure mercury lamp) at 25 °C, of MPD with all the aforementioned olefins successfully produced a considerable yield of copolymer.

Physical Data of Cycloadducts and Copolymers. 3-(2-Methylpropenyl)-1,1,2,2-tetracyanocyclobutane: white crystals, mp 134–136 °C. IR (KBr, cm^{-1}): 2255 (CN), 1645 (C=C). ^{1}H NMR ($CDCl_3$): δ 1.82, 1.87 (2CH_3, 2s), 2.90–3.2 (2H, H_4, m), 4.10–4.30 (1H, H_3, q), 5.30–5.40 (1H, vinyl H, d). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.5; H, 4.8; N, 26.6. Found: C, 68.38; H, 4.56; N, 26.57.

3,3-Dimethyl-4,4,5,5-tetracyanocyclohex-1-ene: ^{1}H NMR ($CDCl_3$): δ 1.57, 1.62 (2CH_3, 2s), 3.8–3.9 (2H,H_6, t), 5.75 (2H, H_1, H_2, s).

Mixture of 3,3-dimethyl-4,4-dicyano-5-(methoxycarbonyl)cyclohex-1-ene (one isomer) and 2,2-dicyano-1-(methoxycarbonyl)-3-(2-methylpropenyl)cyclobutane (two isomers) (cycloadducts obtained from the MDA–MPD reaction): yellow crystals, mp 100–115 °C. ^{1}H NMR ($CDCl_3$): δ 1.35, 1.55 (2CH_3 of cyclohexene derivative, 2s), 1.77, 185 (2CH_3 of cyclobutane derivative, m), 4.1 (1H, H_3 of cyclobutane, br, m), 5.5–5.6 (1H, vinyl H of cyclobutane derivative, br, d), 5.7–5.8 (2H, vinyl H of cyclohexene, br, s). Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.42; N, 12.84. Found: C, 66.11; H, 6.40; N, 12.62.

Copolymer of 4-methyl-1,3-pentadiene and methyl β,β-dicyanoacrylate: $T_g = 125$ °C. IR (KBr, cm^{-1}): 2252 (CN), 1738 (C=O), 1640 (C=C). ^{1}H NMR ($CDCl_3$): δ 1.3, 1.5 (2CH_3 of 1,4-copolymer, br), 1.6, 1.8 (2CH_3 of 1,2-copolymer, br), 5.7 (vinyl H of 1,2-copolymer, br), 6.05 (vinyl H of 1,4-copolymer, br). Anal. Calcd for repeat unit $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.42; N, 12.84. Found: C, 65.32; H, 6.25; N, 12.50.

Mixture of dimethyl 3,3-dimethyl-4-cyanocyclohex-1-ene-4,5-dicarboxylate (one isomer) and dimethyl 2-cyano-3-(2-methylpropenyl)cyclobutane-1,2-dicarboxylate (four isomers) (cycloadducts obtained from the DCF–MPD reaction): yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.39, 1.46 (2CH_3 of cyclohexene derivative, 2s), 1.75, 1.83 (2CH_3 of cyclobutane derivative, br, m), 3.9–4.0 (1H, H_3 of cyclobutane, m), 5.4–5.5 (1H, vinyl H of cyclobutane derivative, br, d), 5.65–5.78 (2H, vinyl H of cyclohexene, br, s). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.10; H, 6.76; N, 5.57. Found: C, 61.62; H, 6.42; N, 5.82.

Copolymer of 4-methyl-1,3-pentadiene and dimethyl cyanofumarate: $T_g = 105$ °C. IR (KBr, cm^{-1}): 2245 (CN), 1740 (C=O). ^{1}H NMR ($CDCl_3$): δ 1.2–1.5 (2CH_3 of 1,4-copolymer, br), 1.7–1.9 (2CH_3 of 1,2-copolymer, br), 5.4–5.5 (vinyl H of 1,2-copolymer, br), 5.6–5.8 (vinyl H of 1,4-copolymer, br). Anal. Calcd for repeat unit $C_{13}H_{17}NO_4$: C, 62.10; H, 6.76; N, 5.57. Found: C, 61.59; H, 6.82; N, 5.44.

Copolymer of 4-methyl-1,3-pentadiene and fumaronitrile: T_g = 135 °C. IR (KBr, cm^{-1}): 2246 (CN), 1660 (C═C). ^{1}H NMR (DMSO-d_6): δ 1.2–1.3 (2CH$_3$ of 1,4-copolymer, br), 1.7–1.85 (2CH$_3$ of 1,2-copolymer, br), 5.5–5.8 (vinyl protons, v br). Anal. Calcd for repeat unit $C_{10}H_{12}N_2$: C, 74.94; H, 7.49; N, 17.48. Found: C, 75.27; H, 7.46; N, 17.29.

Copolymer of 4-methyl-1,3-pentadiene and maleic anhydride: T_g = 110 °C. IR (KBr, cm^{-1}): 1855, 1780 (anhydride), 1645 (C═C). ^{1}H NMR (DMSO-d_6): δ 1.2–1.3 (2CH$_3$ of 1,4-copolymer, br), 1.6–1.8 (2CH$_3$ of 1,2-copolymer, br), 5.4–5.7 (vinyl protons, v br). Anal. Calcd for repeat unit $C_{10}H_{12}O_3$: C, 66.58; H, 6.65. Found: C, 65.94; H, 6.63.

Copolymer of 4-methyl-1,3-pentadiene and acrylonitrile: T_g = 130 °C. IR (KBr, cm^{-1}): 2250 (CN), 1650 (C═C). ^{1}H NMR (DMSO-d_6): δ 1.22–1.35 (2CH$_3$ of 1,4-copolymer, br), 1.57–1.77 (2CH$_3$ of 1,2-copolymer, br); 5.4–5.6 (vinyl protons, v br). Anal. Calcd for repeat unit $C_9H_{13}N$: C, 79.94; H, 9.62; N, 10.36. Found: C, 80.16; H, 9.65; N, 10.12.

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