Synthesis and Properties of a New Polymer with a Cubane-Containing Backbone. Synthesis and Metathesis Polymerization and Copolymerization of 1,4-Bis(homoallyl)cubane

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ABSTRACT: The synthesis of an unsaturated polymer containing cubane moieties in the backbone has been achieved by acyclic diene metathesis polymerization of 1,4-bis(homoallyl)cubane. The molecular weight as determined by ^{1}H NMR (6−7 $C_{14}H_{16}$ repeat units) is M_n = 1100−1300. Copolymerization of 1,4-bis(homoallyl)cubane with 1,5-hexadiene gave a polymer fraction containing an average of 9 $C_{14}H_{16}$/6 butenylene repeat units. The copolymer is soluble in THF.

Introduction

Despite their interest as high-energy materials with potential applications in propulsion technologies, there are only a few examples of hydrocarbon polymers containing highly strained polycyclic moieties. Polybenzvalene[1] and poly[1.1.1]propellane,[2] having both strained rings as an integral part of the backbone and a polybutadiene-containing quadricyclane as a pendant group,[3] have been described recently.

Cubane has high density (1.29 g mL^{-1}) and a very high heat of formation (strain energy 690 kJ mol^{-1}). For this reason it has been pointed out that cubane derivatives could have an interesting potential as high-energy materials, and various nitro and nitramino derivatives have been synthesized. On the other hand, cubane-containing polymers may find applications as energetic binders for solid rocket propellants. Polymers with cubane in the backbone or as a pendant group along a polymer chain have been envisioned in this way by Eaton.[4] However cubylcubane and "oligocubanes" have rigid skeletons with high melting points and poor solubility and probably do not fulfill the physical property requirements for an elastomeric binder. We, therefore, reasoned that the presence of a flexible unsaturated hydrocarbon chain between cubyl moieties will yield a more easily processable polymer. Acyclic diene metathesis polymerization, by a step-growth reaction of cubane-containing acyclic dienes with removal of evolved ethylene, could be an interesting approach.[5] Besides, copolymerization with linear unbranched α,ω-dienes, such as 1,5-hexadiene, could improve the physical properties of the final polymer by inserting butenylene units between cubylene moieties within the chain. Moreover co-reaction with a difunctional alkene, such as 3-hexene disilylated diol as described by Grubbs,[6] opens the way to a hydroxy-terminated polymer, which could then be reacted with the readily available cubyl-1,4-diisocyanate[4] to give an elastomeric polyurethane binder. In this paper we describe the synthesis of 1,4-bis(homoallyl)cubane (**1**), its polymerization and copolymerization with 1,5-hexadiene (**2**) using the Schrock molybdenum alkylidene catalyst,[7] and the fractionation and characterization of the products.

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Experimental Section

General Methods. Syntheses and polymerizations were performed under argon atmosphere with vacuum lines and conventional Schlenk tube techniques. Solvents were purified by ordinary methods. ^{1}H and ^{13}C NMR spectra were obtained with Bruker AC200F and MSL400 spectrometers. Polymer structure, copolymer composition, and molecular weights were determined by integration of CH_2 α to cubane (1.6 ppm), allylic CH_2 (2 ppm), cubane H (3.5 ppm), terminal methylene CH_2=- (5 ppm), internal vinyl H (5.4 ppm), and terminal vinyl H (5.8 ppm) resonances. Differential scanning calorimetry (DSC) was performed under an argon atmosphere with a Mettler TA3000 system with a TC10A computer. The samples were encapsulated in an aluminum pan, and an empty aluminum pan was used as a reference. Heating rates were 5 °C/min. The accuracy of the enthalpy measurement was ±4%.

Gel permeation chromatography (GPC) data were collected using a Waters Associates liquid chromatograph equipped with a Waters 510 pump, a WISP 715 automatic injector, and a Waters 410 differential refractometer. Four PL-GEL (7mm × 30 cm) consecutive linear gel columns were used: 50, 100, 1000, and 10000 Å (porosity 5μm). The eluting solvent was HPLC grade THF at a flow rate of 0.7 mL/min. Molecular weights were referenced to narrow dispersity polystyrene samples ranging in molecular weight from 208 to 295 000.

Cubane-1,4-dicarboxylic acid methyl ester was purchased from Great Lakes Chemical Italiana, and 1,5-hexadiene from Aldrich. The catalyst used in polymerizations, [$(CF_3)_2$MeCO]-(N-2,6-C_6H_3-*i*-Pr)Mo=CHC(Me)$_2$Ph (**3**), was prepared as described.[7] Reduction of cubane-1,4-dicarboxylic acid methyl ester and bromination of the corresponding diol were performed as described in the literature.[8] Allyllithium was prepared as described.[9]

Synthesis of 1,4-bis(homoallyl)cubane (1). To a solution of bis(1,4-bromomethyl)cubane (1.2 g, 4.14 mmol) in diethyl ether (4.5 mL), under argon at 0 °C, was added dropwise a solution of allyllithium (13.7 mmol) in diethyl ether (20 mL). The solution was stirred at 0 °C for 4 h. The mixture was quenched with water (3 mL), extracted with diethyl ether (20 mL), and dried over anhydrous Na_2SO_4, and the solvent was evaporated giving an oily liquid. Distillation of crude **1** (5.10^{-6} Torr) gave a colorless liquid (0.8 g, 90% yield). MS: *m/e* 212 (M, 35). ^{1}H NMR ($CDCl_3$) δ: 5.7−6 (m, 2H), 4.7−5.1 (m, 4H), 3.56 (s, 6H), 1.95−2.15 (m, 4H), 1.6−1.7 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 139 (CH), 114 (CH_2), 59.8 (C), 44.8 (CH), 32.5 (CH_2), 28.7 (CH_2). Infrared (cm^{-1}): 3080 (w), 2960 (s), 2920 (s, sh), 2905 (s, sh), 2840 (m), 1638 (m), 1442 (m), 1430 (w, sh), 1412 (w), 990 (m), 910 (s), 838 (m), 735 (m).

Polymerization of 1. Before polymerization, a solution of **1** in C_6D_6 was dried on a sodium mirror. To a Schlenk tube containing catalyst **3** (20 mg, 0.023 mmol) was added at room temperature a solution of **1** (200 mg, 0.94 mmol) in C_6D_6 (1.5

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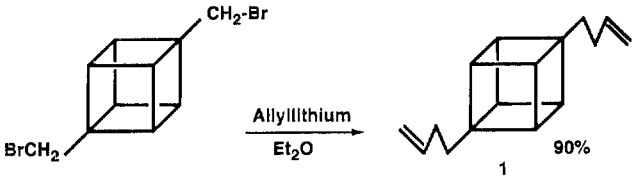
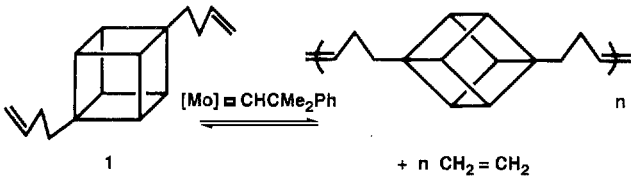
Scheme 1



Scheme 2



mL). An immediate evolution of ethylene was observed. The solution turned from yellow to brown and a white precipitate formed. After 180 min, the polymerization was terminated by adding a drop of pivalaldehyde, and the polymer was isolated by precipitation in methanol (121 mg of solid, 60% yield). ^{1}H NMR ($CDCl_3$) δ: 5.7–6.0 (m, vinyl end group, CH), 5.3–5.6 (m, CH=CH), 4.8–5.1 (vinyl end group, CH_2), 3.57 and 3.56 (s, H from the cubyl group), 1.9–2.1 (m, allylic CH_2), 1.5–1.7 (CH_2).

The polymer was shown to contain an average of 6.2 repeat units from integration data. ^{13}C NMR ($CDCl_3$) δ: 139.2 and 113.9 (CH_2 and CH, vinyl end group), 130.18 (CH, internal double bond), 59.9 (C), 44.9 (CH), 33.1 (allylic CH_2), 32.6 (allylic CH_2, from end unit), 28.6 (CH_2 from end unit), 27.5 (CH_2). Softening point: 190°C. Infrared (KBr, cm^{-1}): 2960 (s), 2900 (s), 2835 (s), 1663 (w), 1635 (m), 1440 (s), 1425 (m), 1315 (m), 1260 (m), 1070 (m), 1035 (m), 970 (s) trans olefin, 910 (s), 835 (s), 800 (m), 750 (w).

Copolymerization of 1 with 2. **1** (193 mg, 0.912 mmol) and **2** (75 mg, 0.908 mmol) were dissolved in benzene (3 mL), and the solution was dried on a sodium mirror. The benzene solution was added, at room temperature, to a Schlenk tube containing catalyst **3** (15 mg, 0.018 mmol). Because of the instability of molybdamethylidene species generated at the begining of the reaction, after 22 h of reaction time, an additional aliquot of **3** (15 mg) was added to reinitiate polymerization. After 48 h of reaction time, the catalyst was deactivated and the reaction mixture treated with methanol (20 mL) and centrifuged. The liquid phase was evaporated to give a pasty solid (57 mg), possessing an average of 4 repeat units (butenylene:cubylene = 1.7:1). The precipitate (119 mg) was analyzed by NMR ($CDCl_3$) and GPC (THF). ^{1}H NMR ($CDCl_3$) δ: 5.7–6.0 (m, vinyl end group, CH), 5.3–5.6 (m, CH=CH), 4.8–5.1 (vinyl end group, CH_2), 3.56 and 3.55 (s, H from the cubyl group), 1.9–2.1 (m, allylic CH_2), 1.5–1.7 (CH_2).

The copolymer was shown to contain an average of 14 repeat units from integration data (butenylene:cubylene = 0.56:1). The number-average molecular weight value of this copolymer, calculated from the proton NMR spectrum (M_n = 2000), agreed quite well with the GPC molecular weight determination using polystyrene calibration (M_n = 2478, M_w = 4070, polydispersity 1.64). The softening point was 90–100 °C. Infrared (KBr, cm^{-1}): 2970 (s), 2910 (s), 2840 (s), 1665 (w), 1640 (m), 1448 (s), 1432 (m,sh), 1310 (m), 1262 (m), 1080 (m), 1040 (m), 970 (s), 912 (m), 840 (s), 805 (m), 750 (w), 725 (w), 700 (w).

Results

The main step for synthesis of **1** is described in Scheme 1. As for most metathesis polymerization of acyclic dienes, the polymers produced were found to be oligomers; however, we refer to these oligomers as "polymers". Homopolymers were not readily soluble in ordinary solvents, and only a small concentration of polymer was dissolved in $CDCl_3$ for ^{1}H and ^{13}C NMR determinations (Figure 1 and Figure 6a).

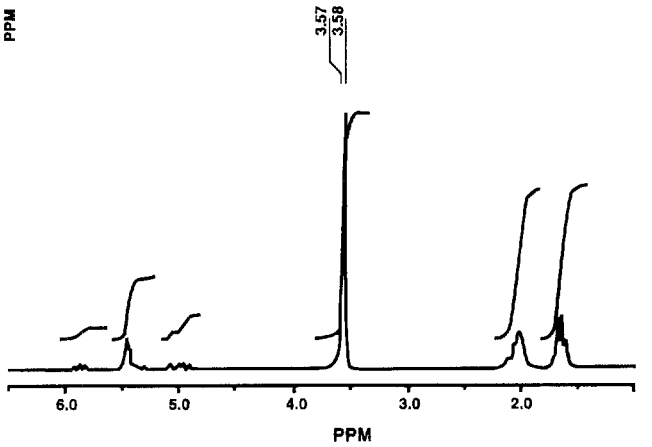


Figure 1. ^{1}H NMR spectrum of 1,4-bis(homoallyl)cubane homopolymer.

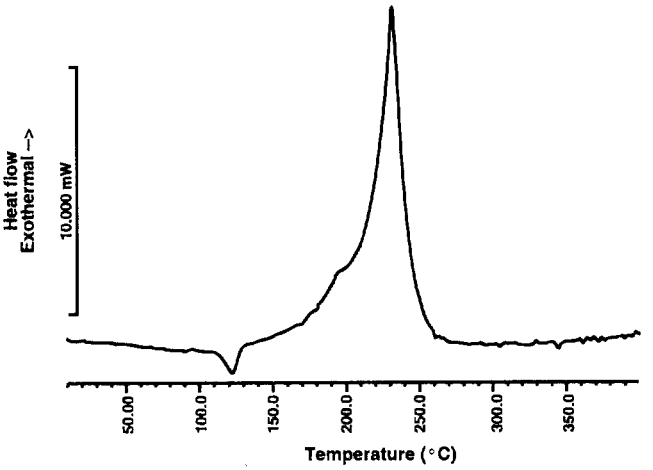


Figure 2. DSC thermogram of 1,4-bis(homoallyl)cubane homopolymer at 5 °C/min.

The ^{13}C NMR spectrum exhibits, in the sp^2 carbon region, only one internal olefin signal at 130.18 ppm, indicating a high degree of stereochemical purity, and two small terminal olefin signals at 113.9 and 139.2 ppm, showing a relatively low degree of polymerization. The stereochemistry of the polymer is assumed to be trans according to the ^{13}C NMR signal at 130.18 ppm.[10,11] The infrared spectrum also confirms the trans stereochemical assignment. The structure of this polymer corresponds to the expected reaction (Scheme 2). We refer to this repeating unit as a "cubylene" moiety.

^{1}H NMR end group analysis (integration of the terminal versus internal olefin signals) gave an average of 6.2 repeat units ($C_{14}H_{16}$ = 184). The number-average molecular weight, M_n, calculated from this value is in the 1100–1200 range.

A DSC thermogram of the homopolymer (Figure 2) did not show any glass transition or any other transitions, but an exothermic peak between 180 and 260 °C (1890 J/g) was observed, which corresponds to 348 kJ for each $C_{14}H_{16}$ repeat unit, i.e., 615 kJ for each cubane moiety.

On account of the low solubility and high softening point (190 °C) of the polymer of **1**, we turned to its copolymerization with **2**, thus inserting some butenylene units between cubylene moieties. The presence of a flexible butenylene unit accounts for the solubility of the copolymer. The copolymerization was performed using first an equimolar ratio of **2** and **1** and then a roughly 2-fold excess of **1**.

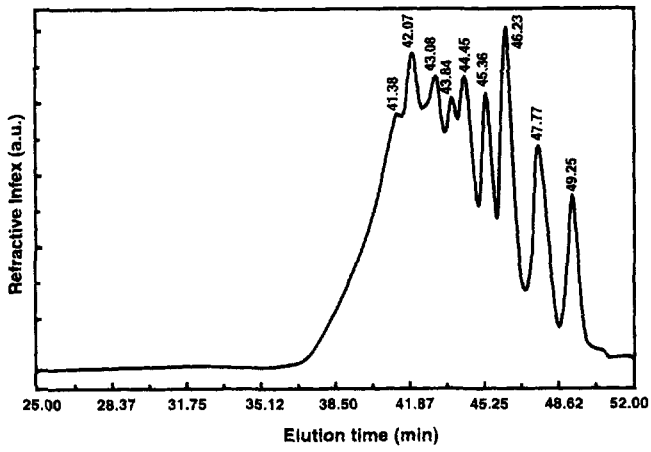


Figure 3. GPC trace of the crude copolymerization product of 1,4-bis(homoallyl)cubane and 1,5-hexadiene: [1] = [2] = 0.3 M, ([1] + [2])/[Mo] = 50; Total sample, $M_n \approx 690$, $M_w \approx 1090$, PDI ≈ 1.58).

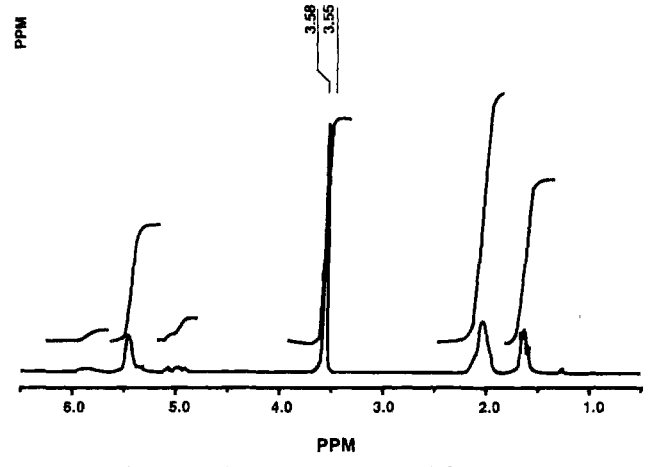


Figure 4. ^{1}H NMR ($CDCl_3$) spectrum of the purified fraction P1 of the 1,4-bis(homoallyl)cubane and 1,5-hexadiene copolymer: butenylene/cubylene = 0.53; average number of repeat units 12.

With the first feed, the crude copolymer obtained after evaporation of the solvent was a viscous pasty solid soluble in various organic solvents (benzene, tetrahydrofuran, chloroform, etc.). Investigation by GPC (Figure 3) showed a broad molar mass distribution in the 250–2200 range. The presence of several peaks is probably due to a mixture of homopolymers and copolymers.

The crude copolymer was fractionated by precipitation with methanol. The first precipitate was purified by dissolution in dichloromethane and reprecipitation with methanol, yielding a white solid P1. The concentration of the corresponding mother liquor led to a pasty solid P2, and a viscous oil P3 was obtained by evaporation of the mother liquor corresponding to the first precipitation.

As shown in Figure 4, the enhancement of the signal corresponding to the allylic protons is the result of the presence of butenylene units in the purified copolymer fraction P1.

The single peak observed in the GPC trace of this fraction (Figure 5) is more in favor of a copolymer than of a blend of homopolymers. The number-average molecular weight values of these copolymers, calculated from the proton NMR integration data, agreed well with the GPC molecular weight determinations using polystyrene calibration. (Table 1).

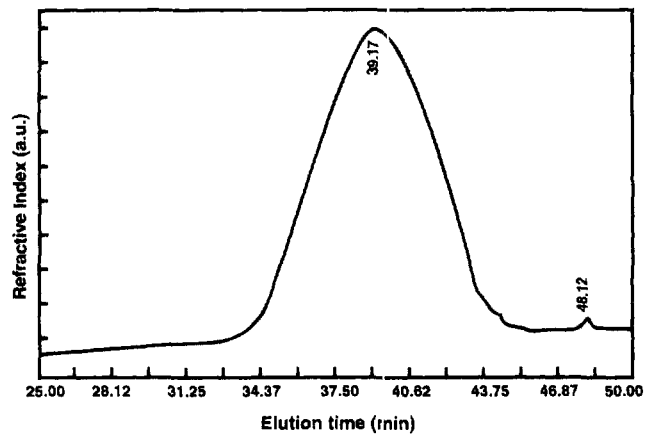


Figure 5. GPC trace of the purified fraction P1 of the 1,4-bis(homoallyl)cubane and 1,5-hexadiene copolymer: ([1]/[2] = 1, [1] = [2] = 0.3 M, ([1] + [2])/[Mo] = 50; $M_n \approx 2480$, $M_w \approx 4070$, PDI ≈ 1.64).

Table 1. Results of Copolymerization Reactions

monomer ratio **1**:**2**	1	1.8
[monomer]/[catalyst]	50	40
reaction time (h)	24	24
P1 yield[a] (%)	27	26
av no. of repeat units (NMR)	12	10
butenylene/cubylene (NMR)	0.53	0.13
M_n (NMR)	1700	1700
M_n (GPC)	1780	1690
M_w (GPC)	2240	2390
polydispersity	1.26	1.41
P2 yield[a] (%)	31	21
av no. of repeat units (NMR)	10	6
butenylene/cubylene (NMR)	0.92	0.48
M_n (NMR)	1200	900
P3 yield[a] (%)	38	46
av no. of repeat units (NMR)	4	4
butenylene/cubylene (NMR)	1.2	0.7
M_n (NMR)	450	600
M_n (GPC)	nd[b]	570
M_w (GPC)	nd	1026
polydispersity	nd	1.8

[a] Estimated according to the average copolymer composition. [b] nd, not determined.

Figure 6b displays the carbon NMR spectrum of the copolymer fraction P1 of **2** and **1**, which exibits several internal double-bond signals. The expanse of the sp^2 carbon region (Figure 7) reveals the presence of six peaks: (A) 130.68 (medium), (B) 130.15 (large), (C) 129.97 (small), (D) 129.77 (small), (E) 129.47 (medium), and (F) 129.42 (small). Peak B is attributed to the trans "cubylene"–"cubylene" linkage because its chemical shift is very close to the value observed for the sp^2 carbons in the homopolymer (130.18 ppm). Signals F and C are close to the two sp^2 carbon signals of the butenylene homopolymer (cis and trans stereochemistry) reported[11] at 129.4 and 130.0 ppm in $CDCl_3$. These signals can be attributed to the cis and trans butenylene linkage in the copolymer or in the butenylene homopolymer. Even in this last hypothesis, the presence of the other three signals is due to additional linkages between repeat units in the copolymer. The two peaks of medium intensity A and E are probably due to the trans cubylene–butenylene linkage or to the trans butenylene–cubylene linkage.

Owing to the trans stereochemistry of the 1,4-bis(homoallyl)cubane homopolymer, the cis cubylene–cubylene linkage is not expected and the other two possible linkages (cis cubylene–butenylene or cis butenylene–cubylene) are expected to be rare and then to

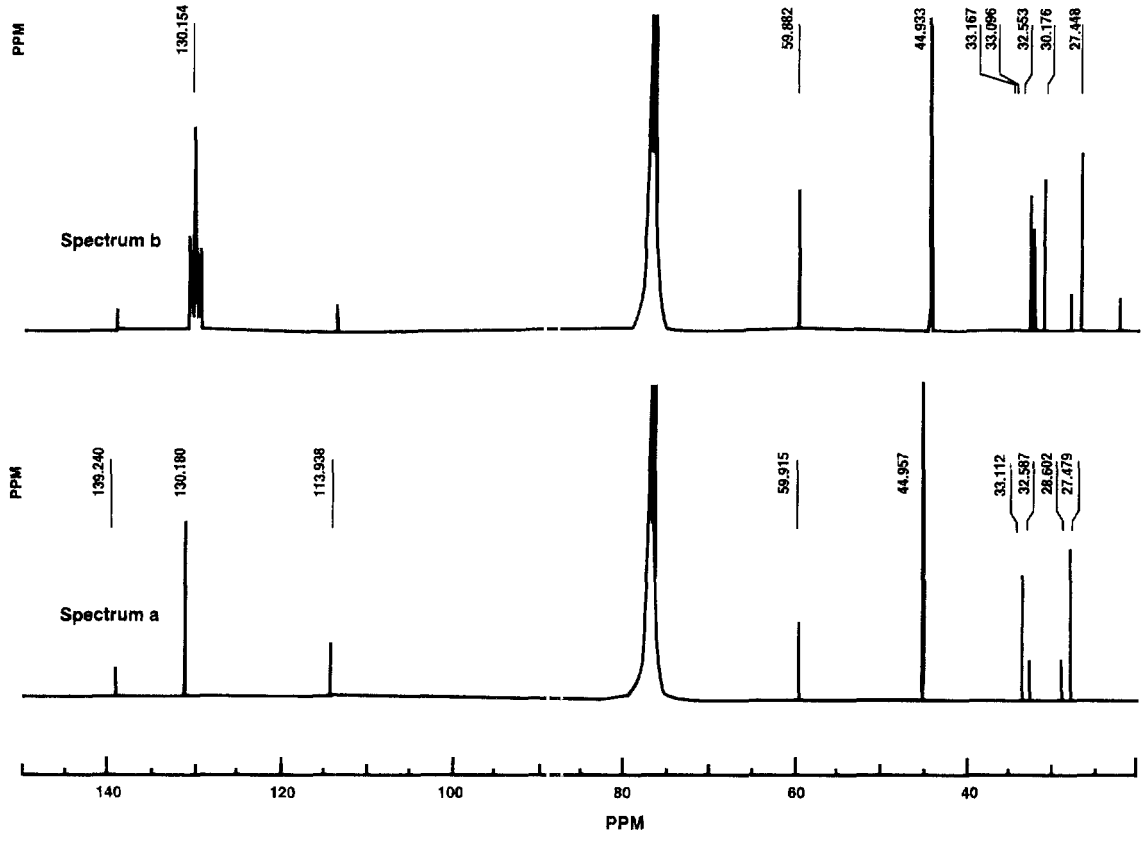


Figure 6. (a) ^{13}C NMR ($CDCl_3$) spectrum of the 1,4-bis(homoallyl)cubane homopolymer; (b) ^{13}C NMR ($CDCl_3$) spectrum of the purified fraction P1 of the 1,4-bis(homoallyl)cubane and 1,5-hexadiene copolymer: butenylene/cubylene = 0.56; average number of repeat units 14.

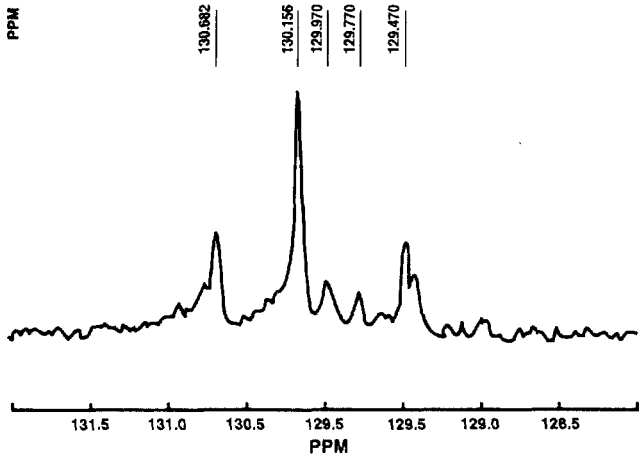


Figure 7. ^{13}C NMR expanse of sp^2 region of spectrum b.

correspond to small peaks.

Due to steric effects, the reactivity of **1** and **2** is expected to be quite different, but our results demonstrate that their copolymerization is possible.

Conclusion

This paper describes an efficient synthesis of a new monomer, 1,4-bis(homoallyl)cubane, and its polymerization and copolymerization with 1,5-hexadiene. Using a non-Lewis acidic metathesis catalyst, we have shown that monomer **1** undergoes polymerization without any rearrangement of the cubane structure.

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