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Polymerization of olefins with bulky substituents. 1. Homo- and copolymerization of 3-(1-adamantyl)propene

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Abstract

The use of bulky substituents like adamantane has been shown in the past to influence the glass transition temperatures of polymers significantly. In this paper the synthesis and homopolymerization of the monomer 3-(1-adamantyl) propene is described, as well as the copolymerization of this monomer with ethene, propene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. The resultant copolymers proved to be largely insoluble in organic solvents. It was also demonstrated that the presence of the bulky methyladamantyl side group influenced the glass transition temperatures of the copolymers in comparison with the corresponding homopolymers.

Keywords: Polymer chemistry; Polymer synthesis

1. Introduction

The incorporation of bulky pendant groups like the adamantyl group has been shown to significantly affect the glass transition temperatures (T_g) of polymers. Adamantyl groups have been placed in polymers as part of the main chain [1–3] and as side groups [4–9]. The use of α-olefins having adamantyl or methyladamantyl substituents have received little or no attention [10–13]. Capaldi and Borchert [10] reported the synthesis of 3-(1-adamantyl)-1-propene and the polymerization thereof to low yield (12.5%) using Ziegler–Natta catalysts. This paper describes the synthesis of the monomer 3-(1-adamantyl)-1-propene (allyl adamantane) (**1**) and the polymerization of **1** with ethene (**2**), propene (**3**), 1-pentene (**4**), 4-methyl-1-pentene (**5**) 1-hexene (**6**), and 1-octene (**7**) (Scheme 1), using a metallocene catalyst system.

2. Experimental

2.1. Materials

The monomers were either purchased form Aldrich and used as received (**2**–**7**) or synthesized (**1**), purified and dried over CaH_2 before use. The catalyst, *rac*-ethylenebis(indenyl) zirconium dichloride was purchased from Aldrich and used as received, as was the cocatalyst, methyl alumoxane (MAO, 10% solution in toluene).

2.2. Methods

All operations involving air- and moisture-sensitive compounds were conducted under a N_2 atmosphere, either by using standard Schlenk techniques or in a PlasLabs dry box. Solvents were stringently dried before use using standard procedures, except for carbon disulfide and ethanol, which were used as received. Glassware was dried overnight at 120 °C before use, assembled hot and cooled under a N_2 atmosphere.

TGA analyses were performed using a SDT simultaneous DTA-TGA (TA Instruments) at a heating rate of 20 °C/min. Glass transition and melting temperatures were obtained using a DSC 2920 differential scanning calorimeter (TA Instruments) at a heating rate of 10 °C/min. FTIR

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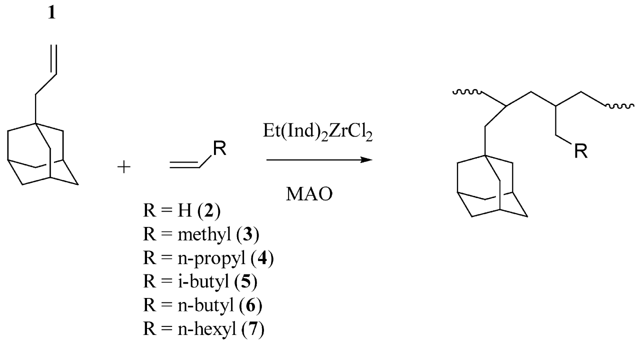


Scheme 1.

spectra were recorded on a Mattson Instruments Galaxy Series FT-IR. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 NMR spectrometer, with $CDCl_3$ as the solvent of choice at ambient temperatures. High temperature NMR analyses were conducted at 100 °C using a 1:10 ratio of a C_6D_6/1,2,4 trichlorobenzene solvent mixture. ^{13}C CP MAS spectra were recorded on the same instrument at ambient temperature.

Where possible the molecular weight was determined by high temperature GPC (HTGPC). Samples for HTGPC were analyzed with a Waters Alkana 2000 GPC at a flow rate of 1.0 ml/min. The analyses were carried out in 1,2,4,-trichlorobenzene at 145 °C and the molecular mass and molecular mass distributions were obtained from this. Each set of samples included a polystyrene standard and a NBS 1475a standard in order to check the validity of data against the calibration curve data.

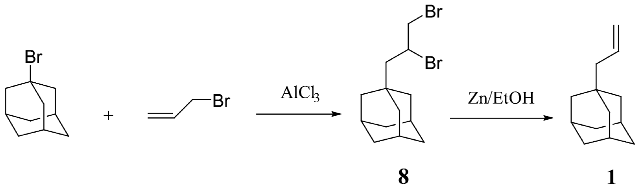
2.3. Monomer synthesis

The target monomer (**1**) was synthesized via the intermediate 1-(1-adamantyl)-2,3-dibromopropane (**8**) (Scheme 2).

2.3.1. 1-(1-Adamantyl)-2,3-dibromopropane (*8*)

1-Bromoadamantane (10.8 g, 50 mmol) and 3-bromo-1-propene (6.05 g, 50 mmol) were dissolved in 40 ml of carbon disulfide. The solution was cooled with stirring to below −70 °C (dry ice/acetone) and $AlCl_3$ (0.5 g, 3.75 mmol) was added in small portions over a period of 20 min. The temperature was then allowed to rise slowly to between −35 and −30 °C and maintained at this temperature for a further hour.

The reaction mixture was then poured into an ice/water mixture and the organic layer was extracted with a large excess of diethyl ether. The organic extract was washed with water, dried over $MgSO_4$ and the solvent removed under reduced pressure. The product was then redissolved in hexanes and repetitively extracted with water to remove the residual carbon disulfide. After further drying over $MgSO_4$ and removal of the solvent, 13.7 g (82%) of 1-(1-adamantyl)-2,3-dibromopropane was isolated. This product was used without any further purification in the next stage. Some of the product was purified by distillation for spectral analysis; ^{1}H NMR ($CDCl_3$): δ (ppm): 4.20 (d), 3.84 (d), 3.56 (t), 2.10 (s), 1.66 (s), 1.60 (s). ^{13}C NMR ($CDCl_3$) δ (ppm): 50.8, 46.3, 42.4, 38.4, 36.9, 32.4, 28.5.



Scheme 2.

2.3.2. 3-(1-Adamantyl)-1-propene

Zinc dust (3 g, 46 mmol) was added to ethanol, and the mixture heated to reflux. To this was added, dropwise over a period of 30 min, the intermediate **8** (13.7 g, 40.8 mmol). When addition was complete, the resulting mixture was refluxed for a further 3 h, washed with water, dried over $MgSO_4$ and the solvent removed to give 3-(1-adamantyl)-1-propene. The product was purified by distillation (>98%, GC), yield 75%. ^{13}C NMR ($CDCl_3$) δ (ppm): 134, 116, 49.2, 42.6, 37.0, 31.1, 28.0. IR (neat) (cm^{-1}): 3070, 2900, 2846, 1640, 1345, 1100, 997, 910, 665.

2.4. Polymerization reactions

2.4.1. Copolymers of *1* with ethene

Copolymerization reactions of **1** with ethene were conducted in a 350 ml Parr autoclave. Typically **1** (0.65 g, 3.7 mmol) was dissolved in 100 ml of dry toluene, added to the reactor and the catalyst, (0.38 μmol in 1 ml of toluene) and methylaluminoxane (4 ml of a 10% solution in toluene) was added. The reactor was sealed and pressurized to a pressure of 300 psi with ethene. The reactor was heated to 80 °C and kept at that temperature for 18 h. The reactor was cooled, vented and the polymer precipitated in acidic methanol (10% HCl). The mixture was stirred for 24 h, filtered, the product well washed with methanol and dried under reduced pressure.

2.4.2. Copolymers of *1* with α-olefins

Typically, 4-methyl-1-pentene (1 g, 11.9 mmol) and **1** (0.8 g, 4.5 mmol) was dissolved in 5 ml of toluene in a Schlenk tube equipped with a magnetic follower, side-arm and stopcock. The reaction mixture was then repeatedly frozen in liquid N_2, evacuated and thawed. After the last freeze-thaw cycle, the reaction mixture was covered with a nitrogen atmosphere. The *rac*-ethylenebis(indenyl)zirconium dichloride (0.7 μmol in 0.5 ml of toluene) was added by syringe, followed by 2.5 ml of a 10% solution of MAO in toluene. The reaction flask was then placed in an oil bath at 40 °C and the reaction mixture stirred for 3 h. The polymer was precipitated in acidic methanol and worked up as described for the ethene copolymers. Yield: 0.96 g (53%).

2.4.3. Homopolymers

Homopolymers of **1** as well as the olefins **4**, **5**, **6** and **7** were prepared by polymerization under inert conditions in a Schlenk tube. Procedures were essentially similar to those described in the section on copolymerization of **1** with the α-olefins.

3. Results and discussion

3.1. Monomer synthesis

The preparation of 3-(1-adamantyl)-1-propene (allyl adamantane) has been reported by a number of authors [10–14]. The method of Sasaki et al. [11] involving the reaction of chloroadamantane with allyltrimethylsilane in CH_2Cl_2 using $TiCl_4$ as catalyst was unsuccessful in our hands. We found the method of Thoma et al. [12] to give only moderate to low yields (30–40%). Similarly attempts to produce **1** by Grignard reactions either via the use of adamantylmagnesium bromide of allylmagnesiumbromide resulted in very low yields ($<15\%$) of the target product. The method described by Borchert et al. [10] (Scheme 2) proved to be by far the most successful. Purification still proved to be difficult, but could be achieved. The final product was obtained in excess of 98% purity, with the impurities being 1-(1-adamantyl) propene and adamantane. It was thought that these impurities would not interfere with polymerization reactions.

3.2. Polymerization reactions

The reaction mixtures and yield for the polymerization reactions are given in Table 1. Reaction temperatures for the polymerization of **1** with the α-olefins **3–7** varied from 35 to 60 °C. The Al/Zr ratio was maintained at 5000:1 for all the reactions.

3.2.1. Homopolymerization reactions

The homopolymerization of **1** proceeded to a good yield to that compared with that reported in the Ziegler–Natta catalyzed polymerization [10]. The powdery polymer product proved to be insoluble in all common organic solvents, even in chlorinated aromatic solvents at elevated temperatures. The polymer showed no melting prior to degradation, but did show a glass transition temperature at 235 °C. The solid state ^{13}C NMR of the polymer is shown in Fig. 1. The peaks associated with the adamantane ring are clearly visible, although the shifts associated with the methylene carbons **b** (see Fig. 1) appear to be split. The backbone carbon **f** is visible where predicted (around 25 ppm), but the backbone carbon **g** (predicted chemical shift 42 ppm) could be hidden beneath the methylene carbon **a** peak. There is a shoulder on this peak (on the upfield side) that could be indicative of carbon **g**.

In addition to the homopolymer of **1**, homopolymers of **2–7** were also synthesized, for comparison with the copolymers of **1** with these monomers. In general, the homopolymers were isolated in good yields, although some difficulty in quantitatively isolating the viscous homopolymers of 1-octene and 1-hexene have resulted in the yield values reported in Table 1 being lower that the actual yields. Melting and glass transition temperatures (T_m and T_g) for the homopolymers are reasonably close to the literature values for the Ziegler–Natta catalyzed poly(α-olefins), with the exception of poly(4-methyl-1-pentene), where the T_m is noticeably lower for the metallocene polymers (210 °C vs. 245 °C).

3.2.2. Copolymerization reactions

The monomer 3-(1-adamantyl)-1-propene was successfully copolymerized with ethene, propene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene.

Copolymers with ethene and propene. The allyl adamantane-ethene copolymers were found to be insoluble in all common organic solvents, and while they exhibited DSC melting points, they showed no visual melting before the onset of degradation. These polymers also showed a glass transition temperature around 10–15 °C, albeit a small transition. No other transitions were observed at lower temperatures. The solid state ^{13}C NMR spectrum clearly indicated the incorporation of 3-(1-adamantyl)-1-propene in

Table 1
Polymerization reaction mixtures, yields, molecular weight and molecular weight distribution (MWD) for the polymerization of **1** with olefins **3–7**

Polymer	**1** (mol%)	α-olefin (mol%)	Temperature (°C)	Yield (%)	M_w (g/mol)	MWD
Poly(1-octene)	0	100	60	55	37,000	2.54
Poly(1-octene-co-**1**)	37	63	60	50	Nd	
Poly(1-hexene)	0	100	60	65	42,000	3.01
Poly(1-hexene-co-**1**)	33	67	60	60	Nd	
Poly(4-methyl-1-pentene)	0	100	45	88	36,500	2.67
Poly(4M1P-co-**1**)-A	28	72	45	53	Nd	
Poly(4M1P-co-**1**)-B	12	88	45	63	Nd	
Poly(1-pentene)	0	100	35	83	31,300	2.31
Poly(1-pentene-co-**1**)	8.5	91.5	35	60	Nd	
Poly(3-adamantyl-1-propene)	100	0	60	55	Nd	

Nd, not done.

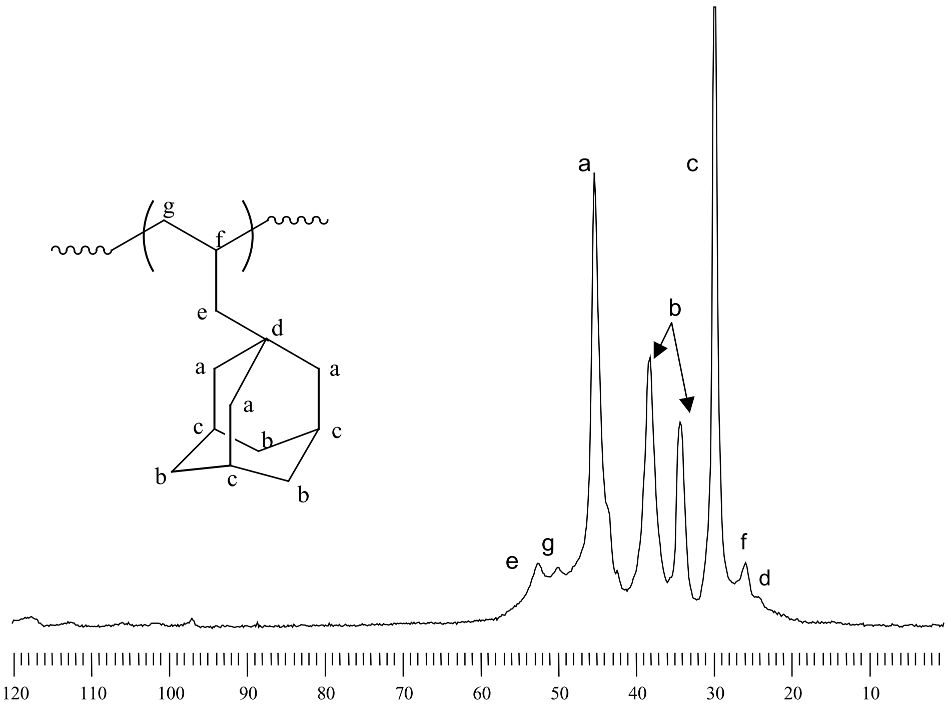


Fig. 1. The solid state ^{13}C NMR spectrum of poly(3-adamantyl-1-propene).

the copolymer. The reason for the infusibility of these materials is unclear. A possibility is the occurrence of crosslinking, but a possible mechanism is not immediately obvious. Similarly, a copolymer of propene and **1** (NMR given in Fig. 2) proved to be insoluble, even at elevated temperatures. The propene-**1** copolymer still exhibited a crystalline melting endotherm, but did not visually melt before the onset of degradation at around 450 °C. In Fig. 2, the visible peaks associated with the adamantane-containing segments of the copolymer are indicated. Other signals are hidden by the strong peaks resulting from the methyl (~20 ppm), methylene (~42 ppm) and methine (~28 ppm) carbons of the polymer chain resulting from propene incorporation.

Copolymers with α-olefins. In all reactions, the yields of copolymer were lower than the corresponding olefin homopolymerization reaction. Nevertheless, reasonable yields were obtained in all cases. Copolymers were largely insoluble in common organic solvents.

The copolymerization of **1** with **7** yielded an amorphous material with a T_g of − 19 °C, which is 54 °C higher than the corresponding α-olefin homopolymer (Fig. 3). Similarly, the T_g of the copolymers of **1** with **6** and **1** with **4** resulted in amorphous materials with T_g values higher than that of the homopolymers. In the case of poly(3-adamantyl-1-propene-co-1-pentene) the melting point present in the 1-pentene homopolymer disappears in the copolymer, making it clear that the presence of the bulky adamantylmethyl substituent severely disrupt the crystallinity as well as influencing T_g. In the case of this copolymer, the T_g is only changed by 10 °C over the homopolymer, but as only 8.5 mol% of **1** was used in this reaction, the incorporation of **1** into the copolymer is probably very limited.

In the case of the copolymerization of **1** with **5**, where the poly(α-olefin) has a glass transition temperature of 45 °C, in the copolymer formed when the concentration of **1** in the reaction mixture was low (12 mol%), the T_g was not affected to a large degree, although the crystallinity was apparently disrupted (evidenced by a lower melting point and decreased heat of fusion). When the concentration of **1** in the reaction mixture was increased to 28 mol%, the resultant copolymer showed no crystallinity whatsoever and a T_g of 69 °C. After heating and fusion, these copolymers appear translucent. The solid-state ^{13}C NMR spectrum of one of these copolymers, compared to the solid state NMR spectra of the respective homopolymers, is shown in Fig. 4. The peaks resulting from the two monomers in the copolymer can clearly be seen in Fig. 4. Of interest here is the disappearance of the strong peak at 33 ppm (methine carbon in the poly(4-methyl-1-pentene) backbone, indicating disruption of long sequences (and crystalline structures) of 4-methyl-1-pentene. The peaks originating from the adamantane ring are indicated by the arrows in Fig. 4; clearly indicating incorporation of the 3-(1-adamantyl)-1-propene in the polymer (Table 2).

4. Conclusions

The homopolymer of 3-(1-adamantyl)-1-propene was successfully prepared using a metallocene catalyst, *rac*-ethylenebis(indenyl)zirconium dichloride with MAO as

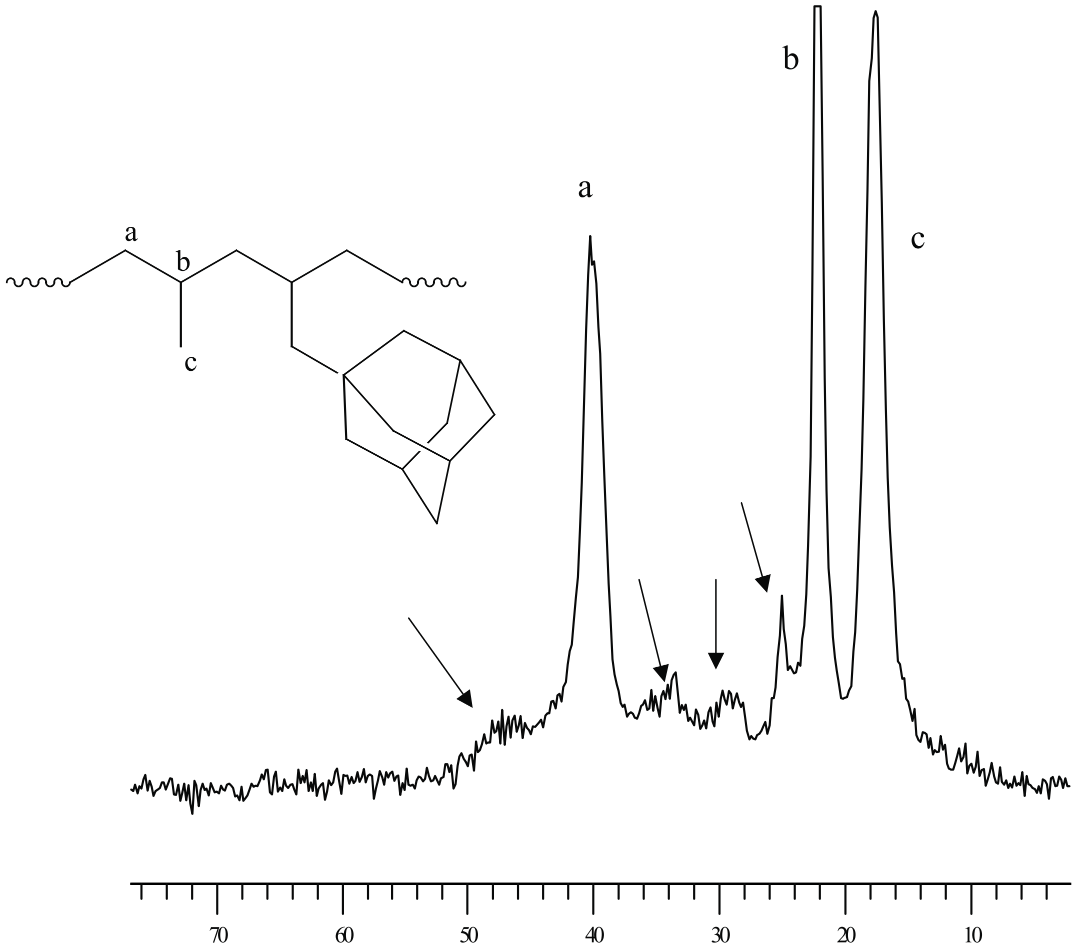


Fig. 2. The solid state ^{13}C NMR spectrum of the copolymer of 3-(1-adamantyl)-1-propene and propene. The peaks associated with the propene sequences are indicated (**a**, **b** and **c**) on the spectrum, while the peaks due to the 3-adamantyl-1-propene are indicated by the arrows.

cocatalyst. In addition, the copolymerization of 3-(1-adamantyl)-1-propene with ethene and a series of α-olefins has been demonstrated. The presence of the bulky methyladamantane pendant group resulted in an increase in T_g for most of the copolymers as well as a disruption of crystallinity. The copolymer of ethene with 3-(1-adamantyl)-1-propene still showed a crystalline melting point (DSC) but did not become fluid prior to the onset of degradation

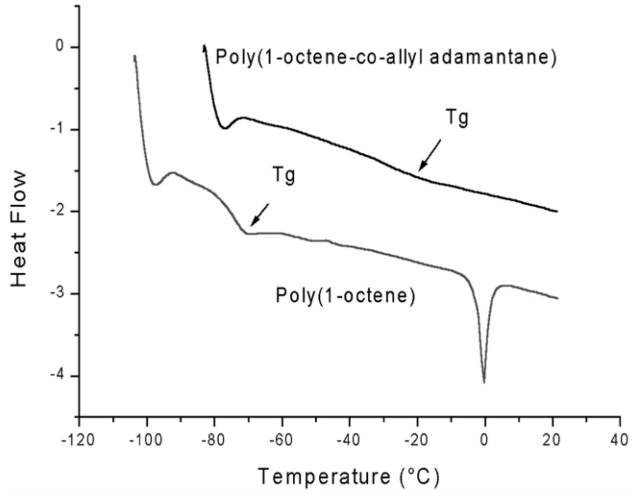


Fig. 3. The DSC scan (third scan) of poly(1-octene) and the copolymer of 1-octene with 3-(1-adamantyl)propene.

Table 2
Glass transition and melting temperatures of homo- and copolymers

Polymer	T_g (°C)	T_m (°C)
Poly(1-octene)	−73	−0.5
Poly(1-octene-co-**1**)	−19	ND
Poly(1-hexene)	−53	ND
Poly(1-hexene-co-**1**)	−13	ND
Poly(1-pentene)	−38	75
Poly(1-pentene-co-**1**)	−25	ND
Poly(4-methyl-1-pentene)	45	210
Poly(4-methyl-1-pentene-co-**1**)-A	69	ND
Poly(4-methyl-1-pentene-co-**1**)-B	47	168
Poly(ethene)	ND	138
Poly(ethene-co-**1**)	12	124
Poly(3-(1-adamantyl)-1-propene)	235	ND

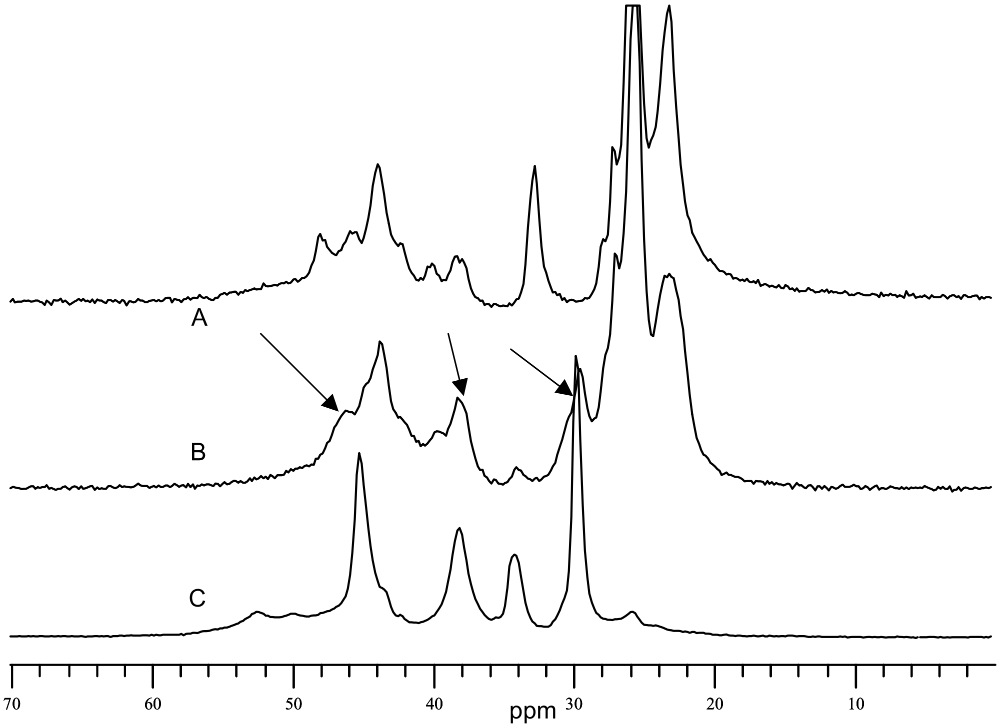


Fig. 4. The solid state ^{13}C NMR spectra of poly(3-adamantyl-1-propene) (C); poly(4-methyl-1-pentene) (A) and a copolymer of 4-methyl-1-pentene and 3-(1-adamantyl)-1-propene (B). Arrows indicate the peaks in the copolymer resulting from the adamantane-containing monomer.

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