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Preparation and Characterization of Graphite-like Pyropolymers from (Z)-1-Methoxy-4-phenyl-1-buten-3-yne

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ABSTRACT: (Z)-1-Methoxy-4-phenyl-1-buten-3-yne was polymerized over $NbCl_5$- or $TaCl_5$-based catalysts followed by pyrolysis to obtain graphite-like pyropolymers. The brown metathesis polymer, poly[(Z)-1-methoxy-4-phenyl-1-buten-3-yne], has the structure of a fully conjugated backbone and was converted into black polyacene-based polymer on pyrolysis. The metathesis polymerization is influenced by substituents directly attached to the acetylene moiety. The structure of polymers is also influenced by oxygen. The polymers were characterized by elemental analysis, GPC, FT-IR, TGA, NMR, laser-Raman, X-ray diffraction, and SEM studies.

Introduction

Linear conjugated polymers such as polyacetylenes, poly(*p*-phenylene), and poly(phenylenevinylene) can be rendered highly conductive by chemical doping.[1-4] The chemical instability of these materials, however, sets a limit on their application to electric and electronic devices, and this limitation promotes interest in the air-stable conducting polymers. Of these candidates, polyacene-based polymers or graphite-like materials have been attracting much interest from basic and applicational viewpoints because of their stability and reversibility during the electrode reactions in the secondary battery.[5] Formation of precursor polymers is very important for making graphite-like structures. We have prepared these polymers by the metathesis polymerization method from acetylene derivatives. There have been many studies on polymerization of various substituted acetylenes by transition-metal catalysts. A number of catalysts based on group 5 and 6 transition metals (Nb, Ta, Mo, W, *etc.*) have been exploited to polymerize substituted acetylenes, especially sterically crowded ones.[6,7] In our previous work, we reported that $NbCl_5$- or $TaCl_5$-based catalyst systems were very effective for selective 1,2-polymerization of asymmetrically substituted diacetylenes, and these polymers were pyrolyzed to give graphite-like conducting polymers which have high conductivities without doping.[8-11] In addition, Masuda *et al.* reported a competing polymerization between phenylacetylene and styrene, suggesting that transition-metal halides can catalyze two different kinds of polymerization, that is, coordination or cationic polymerization. According to this report, triple bonds are more reactive than double bonds in a coordination polymerization pathway, but double bonds are more reactive in cationic polymerization.[12]

In this article, we report the polymerization and pyrolysis of (Z)-1-methoxy-4-phenyl-1-buten-3-yne (MPBEY) to obtain a polyacene-based polymers or graphite-like pyropolymers.

Experimental Section

Instruments. Proton and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AM-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent $CDCl_3$. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC/MS interface by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrophotometer. Thermogravimetric analyses (TGA) were performed under the nitrogen atmosphere at a heating rate of 20 °C/min with a Perkin-Elmer TGA7. The average molecular weight of the polymer was determined in THF solution by a Waters GPC-150C with a calibration curve for polystyrene. The X-ray diffractogram was measured by a Rigaku D/MAX-RC 12 kW X-ray diffractometer using Ni-filtered Cu Kα radiation at a scan speed of 4°/min. The position of the diffraction peaks was calibrated by the peaks of Si powder as a standard. Laser-Raman spectra were obtained using a 514 nm line of an argon ion laser with a back-scattering geometry by a laser-Raman microscope (Jobin-Yvon Ramanor U-1000). SEM was measured by a Phillips 535M.

Materials. (Z)-1-Methoxy-1-buten-3-yne was purchased from Aldrich Chemical Co. and purified according to the

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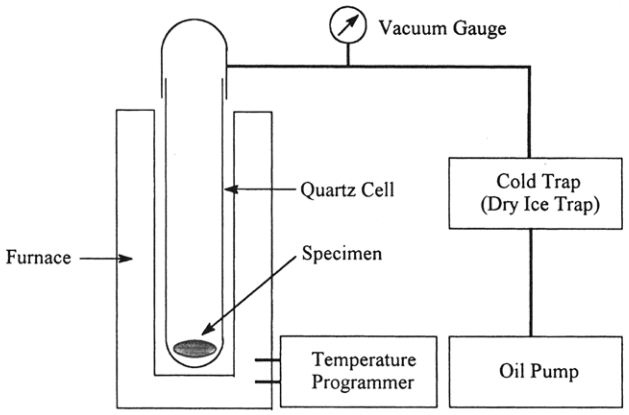


Figure 1. Schematic diagram of a homemade vacuum pyrolysis reactor.

literature procedure prior to use.[13] Bis(triphenylphosphine)-palladium(II) chloride, copper(I) iodide, iodobenzene, $TaCl_5$, and other organometallics as cocatalysts were obtained commercially and used without further purification. $NbCl_5$ was purified by sublimation before use. Solvents were purified by standard methods,[14] care being taken to remove moisture as completely as possible for the polymerization solvent (toluene and chlorobenzene). Solvents of reagent grade were used for chromatography without further purification. A chromatography column of silica gel was prepared with Kieselgel 60 (70–230 mesh).

Synthesis of (*Z*)-1-Methoxy-4-phenyl-1-buten-3-yne (MPBEY). (*Z*)-1-Methoxy-1-buten-3-yne (4.98 mL, 55 mmol) was added to a solution of bis(triphenylphosphine)palladium(II) chloride (702 mg, 1 mmol), copper(I) iodide (381 mg, 2 mmol), and iodobenzene (5.59 mL, 50 mmol) in triethylamine (150 mL) under a nitrogen atmosphere. The mixture was heated and maintained at 30 °C for 1 h. After evaporation of solvent, the reaction mixture was extracted with diethyl ether and separated by column chromatography on a silica gel column using *n*-hexane/diethyl ether (10/1, v/v) as an eluent to give (*Z*)-1-methoxy-4-phenyl-1-buten-3-yne (MPBEY) in 90% yield:[15] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (m, 2H), 7.41 (m, 3H), 6.40 (d, 1H), 4.85 (d, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.2, 133.1, 131.1, 128.2, 127.5, 92.5, 85.1, 83.9, 60.4 ppm; MS (70 eV) *m/e* 158 (M^+, 100), 115 (M^+-C_2H_3O, 83.4).

Polymerization. All the procedures for the preparation of the catalyst system and polymerization reaction were carried out under a dry argon atmosphere. A typical procedure is as follows (Table 2, fourth row): A suspension of $NbCl_5$ (171 mg, 0.63 mmol) and a 0.1 M solution of $(n\text{-}Bu)_4Sn$ in chlorobenzene (6.32 mL, 0.63 mmol) was stirred at 80 °C for 15 min, and a chlorobenzene (58 mL) solution of MPBEY (5 g, 31.6 mmol) was added with continuous stirring at 80 °C for 24 h. Methanol was added to the reaction mixture followed by suction filtration to obtain poly(MPBEY) (2.75 g, 55%), and the product was dried overnight under vacuum at 50 °C.

Vacuum Pyrolysis. Reaction of poly(MPBEY) under vacuum was carried out using a homemade vacuum pyrolysis reactor, as shown in Figure 1. The specimen (about 1 g) was introduced into a quartz cell (inside diameter, 35 mm; length, 400 mm). After the cell was closed, it was evacuated to around 10^{-1} Torr by an oil pump. The specimens were pyrolyzed at a heating rate of 20 °C/min. After reaction under vacuum, the pyroproduct was cooled to room temperature, the vacuum were released, and the product was removed from the cell. The reaction at the highest temperature is controlled exactly for 1 h. The pyropolymers are denoted by poly(MPBEY)–T_p (T_p: pyrolysis temperature).

Results and Discussion

The ratio of weight/number-average molecular weight (polydispersity index, PI) of poly(MPBEY) determined by GPC was about 1.37–2.39 (Table 2), suggesting that this polymerization is homogeneous. The weight-average molecular weight, however, was no more than several thousand, probably due to a degradation reaction of the polymer formed or termination at double bonds in the early stage of polymerization.[16] Interestingly, the average molecular weight was higher when the substituents directly attached to the acetylene moiety were small, as shown in Table 1.

Table 1. Effect of Substituents on the Polymerization of (*Z*)-1-Methoxy-4-R-1-buten-3-yne[a]

	polymer		
R[b]	yield (%)[c]	M_w[d]	PI[d]
–1-naphthyl	20	1656	1.2
$-CH_2Ph$	58	6782	2.8
$-CH_3$	70	insoluble[e]	

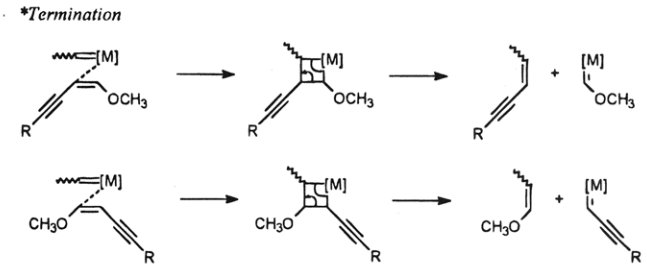
[a] Polymerized in toluene at 80 °C for 24 h; $[M]_0$ = 0.5 M, [cat.] = [cocat] = 10 mM. [b] The structure of the monomer: R–C≡C–CH=CH–OCH_3. [c] The precipitated polymers in methanol were gravimetrically estimated. [d] Values were obtained by GPC analysis with polystyrene standards. [e] Insoluble in any solvent.

Table 2. Polymerization of (*Z*)-1-Methoxy-4-phenyl-1-buten-3-yne[a]

					polymer		
no.	catalyst	$[M]_0$ M	[cat.], mM	[cocat], mM	yield, %[b]	M_w[c]	PI[c]
1	$NbCl_5$·$(n\text{-}Bu)_4Sn$[d]	1	20	100	40	2342	1.37
2	$NbCl_5$·$(n\text{-}Bu)_4Sn$	0.1	3.3	3.3	30	1915	2.14
3	$NbCl_5$·Et_3SiH	1	20	100	35	1941	2.12
4	$NbCl_5$·$(n\text{-}Bu)_4Sn$[e,f]	0.5	10	10	55	2483	1.45
5	$TaCl_5$·$(n\text{-}Bu)_4Sn$[f]	0.1	3.3	3.3	40	2038	2.39
6	$TaCl_5$·Ph_4Sn	0.1	3.3	6.6	28	2322	1.55

[a] Polymerized in toluene at 80 °C for 24 h; structure of the monomer Ph–C≡C–CH=CH–OCH_3. [b] The precipitated polymers in methanol were gravimetrically estimated. [c] Values were obtained by GPC analysis with polystyrene standards. [d] Polymerized in a nitrogen atmosphere; cocatalyst solution was used without deaeration. [e] Polymerized in chlorobenzene. [f] Solubility is low in THF.

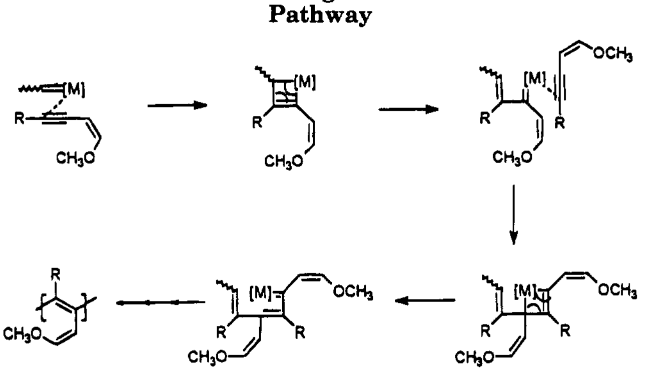
Generally, these monomers have a low reactivity because the competing polymerization between double bonds and triple bonds is involved. Termination started when the number of repeating units reaches approximately 10–15 at the double bonds according to metathesis.[7,17]



Cationic polymerization takes place at the double bonds to a similar extent as the metathesis polymerization at the triple bonds when the solution is not deoxygenated (Table 2, no. 1). When monomer and catalyst solutions are fully deoxygenated by flushing with argon, this oxygen effect is depressed (Table 2, nos. 2–6). Thus the polymerization of the triple bond was depressed in the presence of oxygen, whereas that of the double bond was hardly affected,.[12,18]

The results suggest that triple bonds polymerize through coordination polymerization and double bonds

Scheme 1. Schematic Diagram of the Coordination Pathway



Scheme 2. Schematic Diagram of the Cationic Pathway

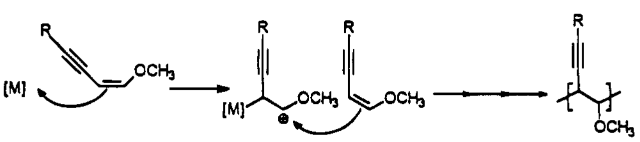


Table 3. Pyrolysis of Poly[(Z)-1-methoxy-4-phenyl-1-buten-3-yne][a]

material[b]	[H]/[C][c]	material[b]	[H]/[C][c]
poly(MPBEY)[d]		poly(MPBEY)−600	0.31
poly(MPBEY)−250	0.59	poly(MPBEY)−700	0.24
poly(MPBEY)−400	0.49	poly(MPBEY)−800[e]	0.19
poly(MPBEY)−500	0.35	poly(MPBEY)−800	0.12

[a] Pyrolyzed *in vacuo* (~10^{-1} Torr) for 1 h. [b] The number after poly(MPBEY) denotes the heat-treatment temperature (T_p). [c] The molar ratio of hydrogen to carbon was determined by elemental analysis. [d] Polymerized in chlorobenzene at 80 °C for 24 h; $[M]_0$ = 0.5 M, [cat.] = [cocat] = 10 mM; structure of the monomer Ph−C≡C−CH=CH−OCH_3. [e] Pyrolyzed *in vacuo* for 30 min.

through cationic polymerization, as shown in Schemes 1 and 2 (though a part of the acetylene moiety participates in the cationic polymerization). The polymerization yield, however, is nearly the same in both cases, as shown in Table 2.

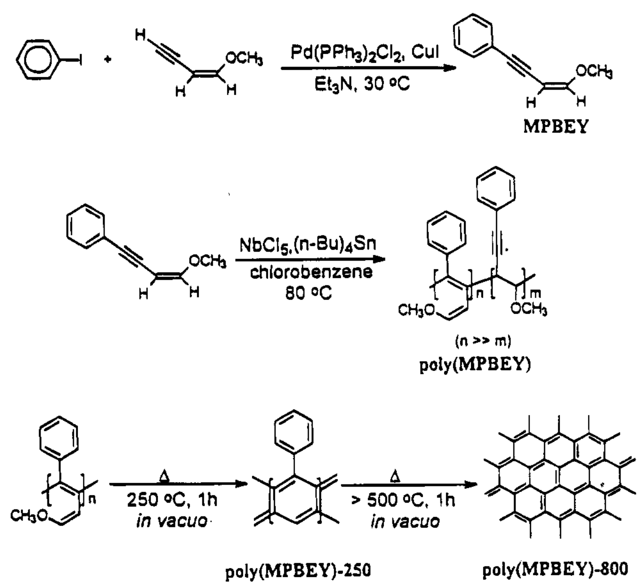
We selected MPBEY as a monomer because this gives the structure of precursor polymer that can be easily converted into polyacene-based polymers, although the polymerization yield was very low.

All the heat-treated pyropolymers were subjected to elemental analysis. The molar ratio of hydrogen to carbon decreased as the pyrolysis temperature was raised, as shown in Table 3. The degree of carbonization can be controlled by the T_p applied, since the H/C molar ratio varies with the pyrolysis temperature (T_p). We can also predict likely structures of the pyropolymers from these results. The exact structures, however, cannot be obtained from these results due to the defect sites of the pyropolymers, which are expected to show different [H]/[C] ratios. The outline of these synthetic routes is suggested as shown in Scheme 3.

Poly(MPBEY) is easily soluble in dichloromethane and tetrahydrofuran, while insoluble in MeOH. Poly(MPBEY)−250, however, is slightly soluble in dichloromethane, and all the pyropolymers prepared over 400 °C are insoluble in any solvent.

Important information on the structure of poly(MPBEY) and heat-treated poly(MPBEY) at various temperatures was obtained from the FT-IR spectra, as shown in Figure 2. The following vibrations are of particular importance: The stretching vibration of the triple bond in the monomer is observed near 2200 cm^{-1} (Figure 2a). When this monomer is polymerized in fully

Scheme 3. Synthetic Routes for Polymer and Pyropolymers



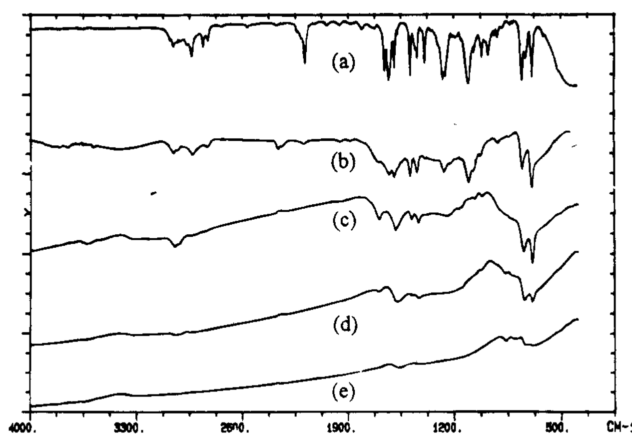


Figure 2. FT-IR spectra of (a) MPBEY, (b) poly(MPBEY), (c) poly(MBPEY)−250, (d) poly(MPBEY)−400, and (e) poly(MPBEY)−500.

degassed chlorobenzene solution by metathesis, this band almost disappears, and this band is absent in the infrared spectrum of poly(MPBEY)−250. A small fraction of unreacted triple bonds is observed in poly(MPBEY) due to end groups. The remaining triple bonds, however, react to give a polyacene-based structure *via* aromatization on pyrolysis. The broad absorption at 1660−1580 cm^{-1} is due to C=C stretching of conjugated double bonds along the main chain and side chain. Its intensity is stronger than that of any other polyacetylene-type polymers probably due to the Fermi resonance between the side groups (Figure 2b). Aliphatic C−H stretching bands near 2900 cm^{-1} and the C−O stretching band near 1100 cm^{-1} almost disappeared upon pyrolysis at 250 °C. This is attributed to loss of MeOH from the pendant group in poly(MPBEY). MeOH and several secondary fragments were identified by the dry-ice trapping method and ^{1}H NMR study. The sample turned black on pyrolysis from originally brown poly(MPBEY). In the spectrum of poly(MPBEY)−250, the aromatic C−H stretching band near 3053 cm^{-1} and the C=C stretching band near 1592 cm^{-1} are clearly observed (Figure 2c). These bands and out-of-plane bands of aromatic C−H near 800 cm^{-1} decreased as T_p was raised to 400 °C (Figure 2d). Since all the characteristic bands vanished when the pyrolysis temperature

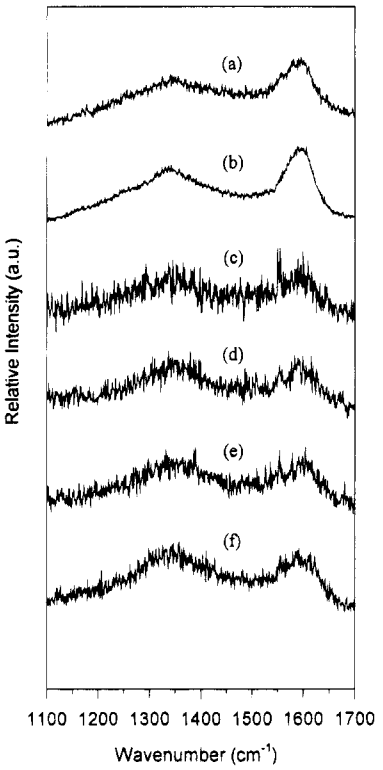


Figure 3. Laser-Raman spectra of (a) poly(MPBEY)−400, (b) poly(MPBEY)−500, (c) poly(MPBEY)−600, (d) poly(MPBEY)−700, and (e) poly(MPBEY)−800 for 30 min and (f) for 1 h.

was raised over 500 °C (Figure 2e), the laser-Raman method was utilized to characterize the polymer.

Figure 3 shows changes of laser-Raman spectra of poly(MPBEY) on heat treatment at various temperatures. The spectrum of crystalline graphite comprises a single first-order line at ~1580 cm^{-1} due to the E_{2g} vibration mode of the graphite lattice, and second-order doublet bands at ~2695 and ~2735 cm^{-1} plus weak features at ~2440 and ~3250 cm^{-1}. Additional bands appear at ~1350 and ~1630 cm^{-1} for imperfect graphites and disordered carbon and sometimes ≈2950 cm^{-1} as a result of the relaxation of symmetry selection rules.[19] A graphite-like structure has also been known to show distinct bands at 1350 and 1630 cm^{-1}. The former corresponds to the A_{1g} vibration mode which becomes Raman active because of the finite size of the graphite crystallites. The latter is due to structural defects of the graphite crystal. As there is a peak at ~1350 cm^{-1}, these specimens are constructed with small crystallites of graphite. All the pyropolymers reacted at T_p's between 400 and 800 °C exhibit broad peaks at around 1630 and 1350 cm^{-1}, indicating the disordered graphite structure. These results suggest two competing processes, carbonization and graphitization. Carbonization implies the thermal decomposition and reaction of the starting materials that generate carbon materials with the disordered graphite structure. In the vacuum pyrolysis of poly(MPBEY), the polymer is considered to be highly hindered for graphitization and it is impossible to form a highly-oriented pyrolytic graphite structure without catalysts such as nickel because of the easy carbonizing character.[20] In the spectrum of poly(MPBEY)−400 and −500 (Figure 3a,b), the intensity of the 1350 cm^{-1} band is smaller than that of the 1600 cm^{-1} band. When T_p is raised to 800 °C, the intensity of the two bands becomes about the same.

Figure 4 shows the TGA of poly(MPBEY), indicating

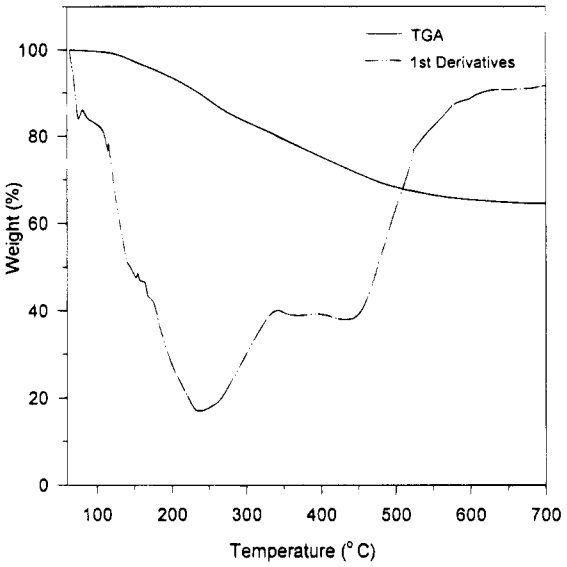


Figure 4. TGA of poly(MPBEY) (heating rate 20 °C/min, N_2 atmosphere).

20.3% weight loss, which corresponds to loss of MeOH when T_p is raised near 340 °C. A lower pyrolysis temperature is required to obtain the same effect under a vacuum. The loss of MeOH is detected from the pendant group of poly(MPBEY) at 250 °C.

Additional information about the structure of poly(MPBEY) and poly(MPBEY)−250 was obtained from ^1H NMR spectra, as shown in Figure 5. In poly(MPBEY) prepared by metathesis in the aerated solution, a broad peak at 6−8 ppm corresponding to the vinyl and phenyl protons appears, while the peak near 3.44 ppm is due to the methoxy protons. Another broad peak near 3.00 ppm is attributed to the methoxy proton and methine protons which is developed because of cationic polymerization pathway (Figure 5a). When MPBEY was polymerized in the fully degassed solution, this band almost vanished (Figure 5b). Poly(MPBEY) produced in the latter solution is structurally more favorable to pyrolyze and in the ^1H NMR spectrum of poly(MPBEY)−250 pyrolyzed *in vacuo* for 30 min, the peak at 3.44 ppm has almost vanished (Figure 5c). This peak is completely exhausted when the pyrolysis is performed for 1 h (Figure 5d). In these spectra (Figure 5c,d), the solvent peaks of TMS, H_2O, and $CDCl_3$ were detected because the solubility is very low. Figure 6 shows the ^{13}C NMR CP/MAS spectra of poly(MPBEY) and poly(MPBEY)−250. The peaks at 120−150 ppm (Figure 6a) correspond to the sp^2 carbons of the polymer backbone and the vinyl and the phenyl groups of the side chains, while the peak at 55.8 ppm is due to the methoxy carbons of the side chains. Because the precursor polymer of poly(MPBEY)−250 has a low molecular weight, the small peak of the acetylene end group is shown at 86.0 ppm. In the spectrum of poly(MPBEY)−250 (Figure 6b), the peaks at 55.8 and 86.0 ppm have completely vanished. If the carbonization is accomplished, the spectrum has the broad line width of the peak and the extent of the upfield tail part for the sample prepared at high T_p indicates that the condensed aromatic rings constructing the material have various structures in the low-conductive parts and/or in the metallic islands due to a Knight shift.[21] In the spectrum of poly(MPBEY)−250, however, only the peak tailing to the 141−142 ppm is detected, suggesting that this pyropolymer has the polyacene structure but not a complete graphite-like structure. This also supports the

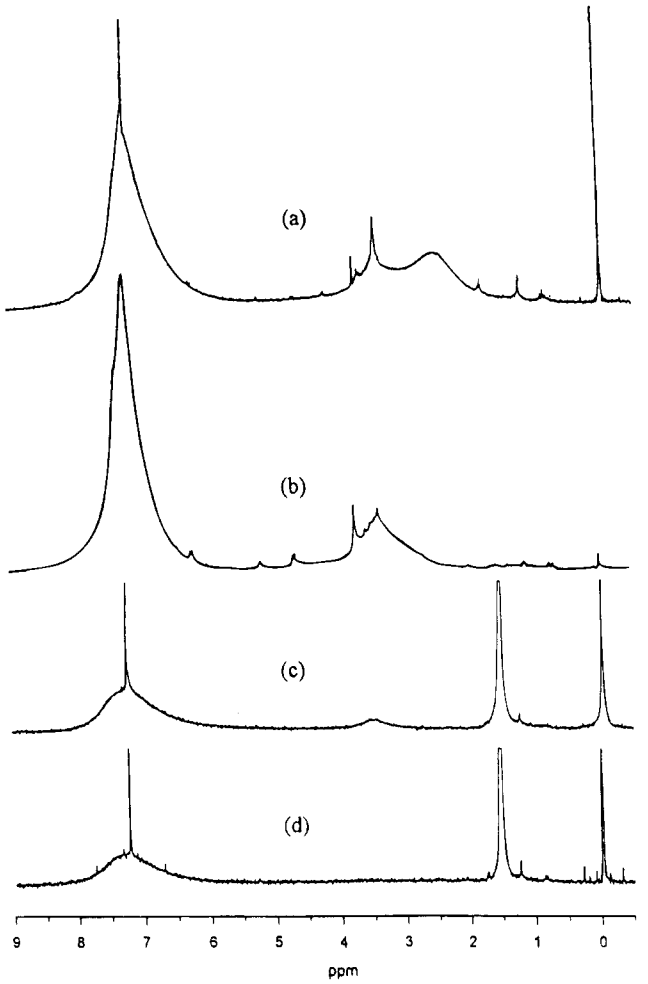


Figure 5. ^{1}H NMR spectra of poly(MPBEY) polymerized (a) in the solution having oxygen and (b) in the fully degassed solution with Ar and of (c) poly(MPBEY)−250 pyrolyzed for 30 min and (d) for 1 h.

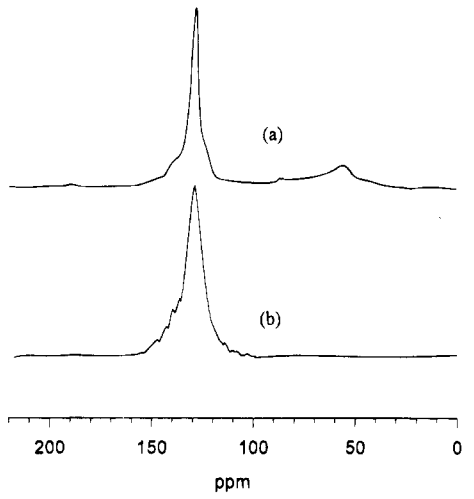


Figure 6. Solid-state ^{13}C NMR CP/MAS spectra of (a) poly(MPBEY) and (b) poly(MPBEY)−250.

loss of MeOH from the side chain of the polymer. In general, the peaks of the sp^2 carbon appear around 127−137 ppm for the phenyl group and 141−142 ppm for the polyacene structure, as calculated by Kojima.[22]

To check the crystallinity of the polymer, powder X-ray diffraction analysis was carried out on heat-treated poly(MPBEY), as shown in Figure 7. In poly(MPBEY) and heat-treated poly(MPBEY), all the peaks

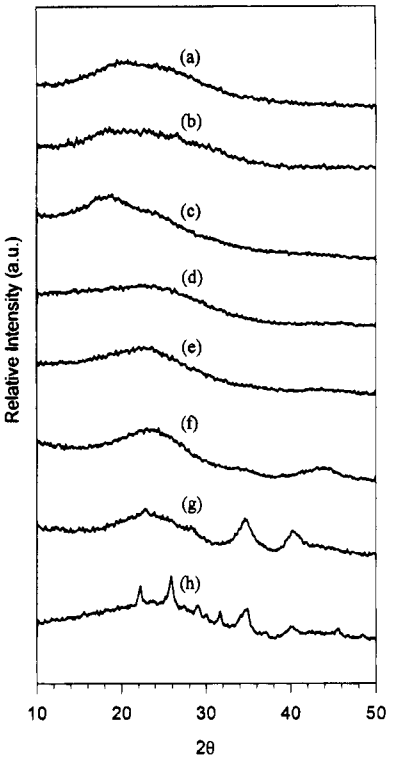


Figure 7. Changes of the powder X-ray diffraction pattern of the polymer and pyropolymers: (a) poly(MPBEY), (b) poly(MPBEY)−250, (c) poly(MPBEY)−400, (d) poly(MPBEY)−500, (e) poly(MPBEY)−600 (f) poly(MPBEY)−700, and (g) poly(MPBEY)−800 for 30 min and (h) for 1 h.

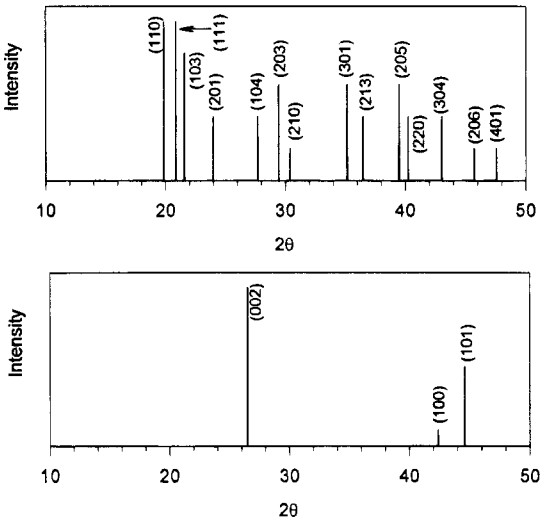


Figure 8. X-ray diffraction pattern of carbon (chaoite) and graphite.

have broad shapes, indicating that this sample is amorphous. As T_p was raised to a higher temperature, however, the pyropolymers were gradually arrayed to give a plate structure having a shorter interlayer distance, although the whole structure is still amorphous. This result is similar to that reported by Tanaka.[23] When the poly(MPBEY) was pyrolyzed at 800 °C for 30 min, crystallinity increased. From the X-ray diffraction patterns of Figure 7g, three broad peaks at 2θ of around 25, 35, and 41° are observed. According to the standard X-ray diffraction patterns of chaoite, a kind of synthetic carbon (Figure 8a), it is clear that a 2θ of 35° is due to the (301) or (213) band.[24,25] The 2θ of 20−25° is assigned to the (002) band, and 41−43° to both (100) and (101) bands (Figure 8b). Figure

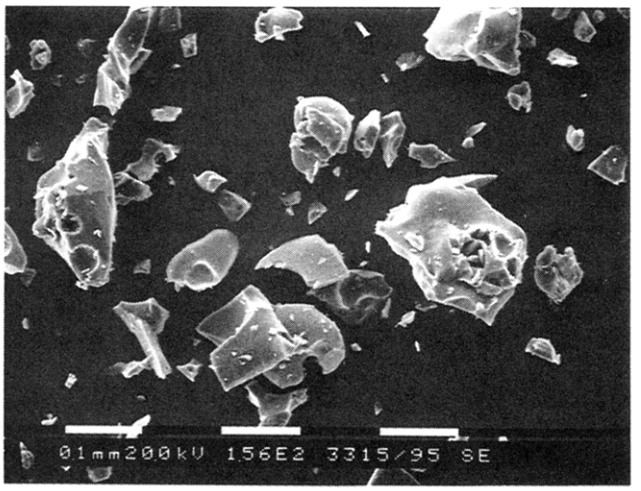


Figure 9. SEM photograph of the poly(MPBEY)−800 for 30 min. The length of white solid-line drawn in the picture is 0.1 mm.

7h shows the X-ray diffraction patterns of semicrystalline graphite-like pyropolymers. Because the pyropolymers have disordered structures, several bands are detected at the other positions at around 25 and 41°. According to these results, these materials have the possibility of application to the electrode of the dischargeable battery, especially a Li battery, and we are in the process of pursuing the electrochemical properties (*e.g.*, intercalation properties) with these pyropolymers.

A SEM (scanning electron microscopy) picture of the particle of poly(MPBEY)−800 for 30 min reveals that it has a platelike structure, as shown in Figure 9. This image is very different from that of PHDO−800 reported by Lee.[9] Poly(MPBEY)−800 has a smooth surface compared to PHDO−800 with a very porous surface. In each particle, the plate is clearly observed, although the ordering is poor when the SEM picture is magnified to observe the morphology of each particle. The final product, poly(MPBEY)−800, is lustrous as a whole.

Conclusions

(*Z*)-1-Methoxy-4-phenyl-1-buten-3-yne (MPBEY) was polymerized to give poly(MPBEY) by metathesis polymerization over $NbCl_5$-based catalysts. This precursor polymer was easily converted into polyacene-based or graphite-like pyropolymers on vacuum pyrolysis. From the results of GPC, FT-IR, laser-Raman, TGA, NMR, X-ray diffraction, and SEM studies, pyropolymers were found to have polyacene structures in which several condensed aromatic rings are present.

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