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Mechano Ions Produced by Mechanical Fracture of Solid Polymer. 5. Cationic Polymerization of Isobutyl Vinyl Ether Initiated by the Mechano Cation of Poly(vinylidene fluoride)

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) was fractured with isobutyl vinyl ether (IBVE) by using a vibration glass ball mill in vacuum in the dark at 77 K. Poly(vinyl isobutyl ether) (PVIBE) homopolymer ($\bar{M}_w = 6.2 \times 10^4$, $\bar{M}_n = 2.3 \times 10^4$) was obtained in the mixture. This result suggests that mechano cations were produced by heterolytic bond scission of carbon–carbon bonds in the PVDF main chain, and a cationic polymerization of IBVE was initiated by the mechano cations. A mechanism of the cationic polymerization of IBVE is proposed.

Introduction

It has been established that mechano radicals are produced by mechanical fracture of polymers at low temperature.[1-16] The radicals, chain-end-type free radicals, are produced by "homolytic bond scission" of carbon–carbon bonds in the polymer main chain. One of the authors (M. S.) has previously reported that radical polymerizations of methyl methacrylate and ethylene were initiated by the mechano radicals in vacuum at 77 K.[17,18]

Recently, we have reported that anions in various fractured polymers are detected by ESR spectroscopy using an electron-trapping technique.[19-22] It was proposed in these reports that "mechano anions" are produced by "heterolytic bond scission" of carbon–carbon bonds in the polymer main chain, and the yield of the mechano anions seems to increase with the polarity of the carbon–carbon bond owing to a substituent group bonded to the carbon in the polymer main chain.[22]

Experimental Section

PVDF (Kynar 720) was dissolved in boiling methyl ethyl ketone with 33% (volume) acetone, cooled, filtered, dried in vacuum at room temperature for 3 days, and further dried in vacuum at 323 K for 9 h. IBVE (Tokyo Kasei Co Ltd.) was washed with a 10% aqueous solution of sodium hydroxide, separated from the aqueous solution, boiled on sodium metal for 1 h, and distilled. The IBVE was degassed by freeze–pump–thaw on sodium metal, distilled 2 times at 243 K, and contacted with PVDF under vacuum. Mechanical fractures of PVDF with or without IBVE were carried out by using a vibration glass ball mill under vacuum in the dark at 77 K for 21 h.[8] After milling, the whole ESR sample tube connected to the glass ball mill was placed in liquid nitrogen, and the powdered sample was dropped into the ESR sample tube within 1 s. ESR spectra were obtained at a microwave power level of 0.04 mW and 100-kHz field modulation in the dark at 77 K by a JEOL JES-FE3XG ESR spectrometer (X-band) coupled to a Melcom 70 minicomputer (Mitsubishi Electric Co.).

1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used to calibrate the magnetic field position on the ESR spectra.

In order to eliminate IBVE monomers, the fractured PVDF with IBVE was air-dried for 4 days and further dried under vacuum at room temperature for 31 h. This sample is referred to as "dried sample" in this article. A part of the dried sample was washed with toluene for 7 h by using a Soxhlet extractor. A residue of the extraction was dried in vacuum at room temperature for 31 h. This residue will be referred to as "residue sample". The extract obtained by the Soxhlet extractor was precipitated with methanol, air-dried for 3 days, and further dried under vacuum at room temperature for 2 days. This sample will be called the "extracted sample". A film of the extracted sample for observation of FT-IR spectra was obtained from a KBr disc from benzene solution. In order to eliminate benzene, the film on the KBr disc was dried under vacuum at room temperature for 68 h.

FT-IR absorbance spectra with 50 times accumulation were obtained by a JEOL JIR-100 FT-IR spectrometer using a KBr method at the FT-IR division of the Instrument Center of Nagoya Institute of Technology. The molecular weight of the extracted sample was obtained by gel permeation chromatography using a TOYO SODA HLC-803D GPC.

Results and Discussion

The ESR spectrum (Figure 1) of fractured PVDF without IBVE was observed at a high microwave power level of 0.4 mW with high amplification. Small humps (indicated with arrows) on both sides of the spectrum having a strong broad singlet in the center are called wing peaks. Figure 1 shows wing peaks with a hyperfine splitting constant of 43.0 mT and an inner triplet with about 2.4 mT superposed on the broad singlet in the center of the spectrum. The wing peaks, due to $2A\|$ from two α-F atoms, indicate that homolytic bond scission of the PVDF main chain occurs, which produces a pair of mechano radicals (chain-end-type free radicals): $-CF_2^{\bullet}$ (I)[8,22] and $^{\bullet}CH_2-$ (II). Accordingly, the inner triplet is assigned to the mechano radical of $^{\bullet}CH_2-$.

The ESR spectrum (Figure 2) from the fractured PVDF with IBVE was found to have a large increase of radical concentration even at a power level of 0.04 mW and with lower amplification. Figure 2 shows wing peaks (marked with arrows, observed at 0.4 mW with high amplification) with a hyperfine splitting constant of 43.0 mT and a inner triplet (1:2:1) spectrum with a splitting of 2.2 mT superposed on an unknown broad singlet in the center of the

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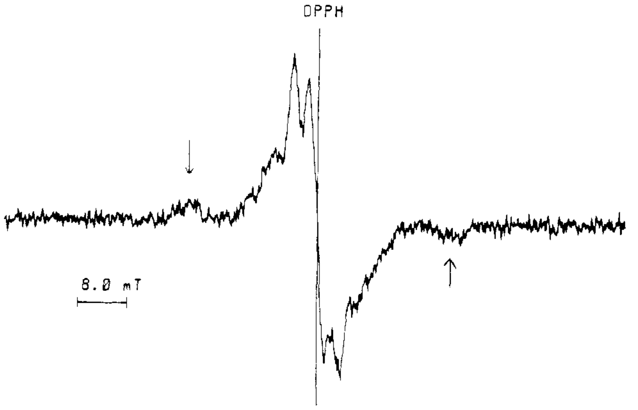

Figure 1. ESR spectrum from PVDF fractured without IBVE in the dark in a vacuum at 77 K (ESR spectrum obtained at a high microwave power level of 0.4 mW). Arrows indicate wing peaks due to $2A_\parallel$ from two α-F atoms. DPPH is used to calibrate the magnetic field position on the ESR spectrum.

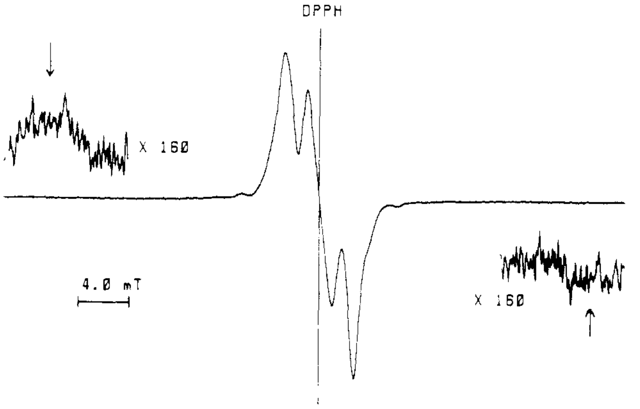

Figure 2. ESR spectrum from PVDF fractured with IBVE in the dark in a vacuum at 77 K (ESR spectrum obtain at 0.04 mW). Arrows indicate the wing peaks observed at 0.4 mW with high amplification.

spectrum. The wing peaks indicate that homolytic bond scission of the PVDF main chain occurs even in the presence of IBVE and produces the mechano radicals, I and II. Since the ESR intensity of the wing peaks in Figure 2 was identical with that found for fractured PVDF without IBVE, mechano radical I was not responsible for the large increase in radical concentration, and therefore, the yield of homolytic bond scission is unaltered even in the presence or absence of IBVE.

The total radical concentration of the fractured PVDF with IBVE is about 11 times greater than that of the fractured PVDF without IBVE, with most of the increase in intensity being due to the inner triplet. These results suggest that an ion produced by mechanical fracture converts to radicals, which causes an increase in the total radical concentration and an increase in the intensity of the inner triplet. It is reported that a vinyl ether monomer behaves as an electron donor at the initiation reaction of a cationic polymerization and converts to a cation radical.[23,24] In addition, IBVE monomer undergoes a cationic polymerization.[25-27] Therefore, our results strongly suggest that the increased radicals are arising from IBVE cation radicals. The triplet spectrum is assigned to the superposed spectrum of two radicals: One is the end radical having a propagating cation of IBVE at the opposite end, $^{\bullet}CH_2–CH(OCH_2CH(CH_3)_2)$- - -$CH_2–C^{+}H(OCH_2CH(CH_3)_2)$ (III), which has a hyperfine splitting constant of 2.2 mT from two equivalent α-protons and very small splitting from one β-proton. The small β-proton splitting seems to be due to a twisting of carbon bonds in the main chain arising from an intrinsic steric hindrance. The other is radical II which is produced by donation of an electron from IBVE to the cation.

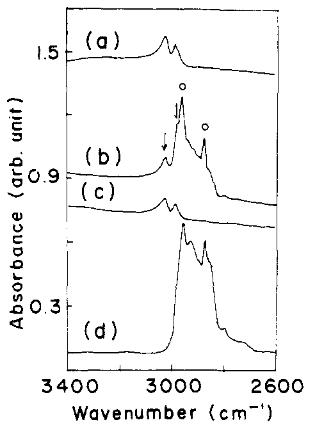

Figure 3. FT-IR spectra in the range 2600–3400 cm^{-1}. (a) PVDF fractured without IBVE; (b) dried sample, arrows and circles show the absorption bands from methylene and the methyl group; (c) residue sample; and (d) extracted sample. The spectral base lines have been offset vertically to avoid overlap.

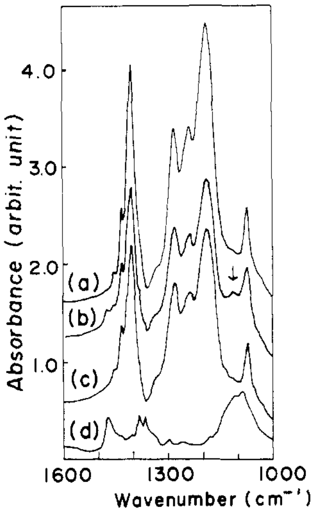

Figure 4. FT-IR spectra in the range 1000–1600 cm^{-1}. (a) PVDF fractured without IBVE; (b) dried sample, an arrow shows absorption band from aliphatic ether group; (c) residue sample; and (d) extracted sample. The spectral base lines have been offset vertically to avoid overlap.

No ESR signal was observed from unfractured PVDF with IBVE, which indicates that the free-radical concentration is induced by scissions in the PVDF main chain.

It was reported[28] by Kamachi et al. that IBVE can react with radicals induced by di-*tert*-butyl peroxide at high concentration when photoirradiated at 365 nm, resulting in PVIBE free radicals. The ESR spectrum (1:2:1:1:2:1) of a doublet of triplets observed from the IBVE free-radical species was postulated to arise from $–CH_2–\dot{C}H(OCH_2CH(CH_3)_2)$. The ESR pattern and the hyperfine splitting constants observed by Kamach et al. are very different from that found in the present study for fractured PVDF with IBVE. Therefore, their postulated mechanism of free-radical formation due to IBVE is different from that indicated by our results.

FT-IR spectra from the fractured PVDF without IBVE show characteristic absorption peaks at 3022 and 2981 cm^{-1} arising from the methylene group shifted by fluorine atoms (Figure 3a) and an absorption band of around 1200 cm^{-1} arising from an aliphatic fluorine atom (Figure 4a). FT-IR spectra from the dried sample show absorption peaks from a methylene group (Figure 3b with arrows), absorption

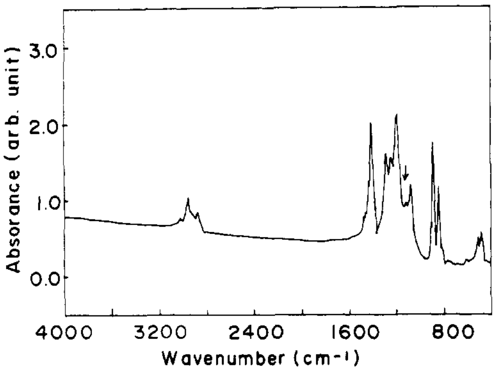

Figure 5. FT-IR spectrum from the dried sample in the range 400–4000 cm^{-1}. An arrow shows absorption band from an aliphatic ether group.

peaks at 2956 and 2873 cm^{-1} (Figure 3b with circles) arising from a methyl group, and absorption peaks at 1113 cm^{-1} arising from an aliphatic ether (Figure 4b with arrows). A FT-IR spectrum of the entire absorption range (400–4000 cm^{-1}) obtained from the dried sample is shown in Figure 5. Since IBVE containing methyl and aliphatic ether groups was eliminated by vacuum drying, the appearance of their absorption peaks indicates the presence of a macromolecular substance. In the FT-IR spectra of the residue sample (Figure 3c and Figure 4c), the absorption peaks arising from methyl and aliphatic ether groups have completely disappeared, with the FT-IR spectrum converting to that found for PVDF fractured without IBVE (Figure 3a). This result indicates that the macromolecular substance was eliminated by washing with toluene, and the substance was a homopolymer having methyl and aliphatic groups. FT-IR spectra from the extracted sample (Figure 3d and Figure 4d) show the presence of characteristic absorption bands arising from methyl and aliphatic ether groups and show the disappearance of an absorption band arising from an aliphatic fluorine atom. The observed spectrum of the extracted sample is identical with that of PVIBE.[30,31] Therefore, the extracted substance is assigned to a homopolymer of PVIBE. The molecular weights of the PVIBE were found by GPC to be $\bar{M}_w = 6.2 \times 10^4$ and $\bar{M}_n = 2.3 \times 10^4$.

The proposed polymerization mechanism of IBVE is depicted by the following:

PVDF fractured with IBVE in the dark in vacuum at 77 K undergoes the following reactions:

$$\text{PVDF} \rightarrow \underset{\text{(I)}}{-\text{CF}_2^{\bullet}} + \underset{\text{(II)}}{{}^{\bullet}\text{CH}_2-} \quad \text{(homolytic bond scission)} \qquad (1)$$

(The mechano radicals are unreactive with IBVE)

$$\text{PVDF} \rightarrow -\text{CH}_2^{+} + {}^{-}\text{CF}_2- \quad \text{(heterolytic bond scission)} \qquad (2)$$

where $-CH_2^+$ is the mechano cation and $^-CF_2-$ is the mechano anion ($^-CF_2-$ is produced by pair formation with $-CH_2^+$)[22]

$$-\text{CH}_2^{+} + \text{CH}_2{=}\text{CH(OCH}_2\text{CH(CH}_3)_2) \rightarrow \underset{\text{(II)}}{-\text{CH}_2^{\bullet}} + {}^{\bullet}\text{CH}-{}^{+}\text{CH(OCH}_2\text{CH(CH}_3)_2) \quad \text{(initiation reaction)} \qquad (3)$$

(IBVE donates an electron to the mechano cation)

$$^{\bullet}\text{CH}_2-{}^{+}\text{CH(OCH}_2\text{CH(CH}_3)_2) + \text{CH}_2{=}\text{CH(OCH}_2\text{CH(CH}_3)_2) \rightarrow \rightarrow \rightarrow \underset{\text{(III)}}{{}^{\bullet}\text{CH}_2\text{-CH(OCH}_2\text{CH(CH}_3))\text{- -CH}_2\text{-}{}^{+}\text{CH(OCH}_2\text{CH(CH}_3)_2)} \quad \text{(propagation reaction)} \qquad (4)$$

(Observed ESR spectrum (shown in Figure 2) is a superposition of radicals I–III.)

It is reported by Stannett and Deffiex[29] that radiation-induced polymerization of super dry vinyl ethers proceeds through a purely free, unpaired, cationic mechanism. Accordingly, the propagation reaction without a counterion, such as reaction 4, is reasonable.

Reaction 3 indicates that one mechano cation produces one radical (II) and one cation radical and results in twice the radical concentration. We have reported that a lower limiting yield of mechano ions (yield of heterolytic bond scissions) in PVDF was 85% using an electron-trapping technique.[22] According to this report,

$$\{[-\text{CH}_2^{+}] + [{}^{-}\text{CF}_2-]\}/\{[\text{I}] + [\text{II}]\} = 85/15$$

$$[-\text{CH}_2^{+}] = [{}^{-}\text{CF}_2-]$$

and therefore,

$$[-\text{CH}_2^{+}] = 5.7\{[\text{I}] + [\text{II}]\}$$

The concentration of the mechano ions is about 5.7 times that of mechano radicals. After the reaction of IBVE, one $-CH_2^+$ produces one radical (II) and one IBVE cation radical. Accordingly, the total radical concentration increases to 11.4 times that of mechano radicals if the mechano cations completely react. The 11-fold concentration increase in this study coincides with the results obtained from the electron-trapping method.[22]

Conclusion

It is concluded that mechanical fracture of PVDF induces heterolytic bond scission of a carbon–carbon bond in the main chain, producing a mechano cation, and that a cationic polymerization of IBVE is initiated by the mechano cation, producing PVIBE homopolymer.

Registry No. PVDF, 24937-79-9; IBVE, 109-53-5; PVIBE, 9003-44-5.

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The Helix-Promoting Ability of Oligo-α-aminoisobutyric Acids at the Carboxyl Termini of Oligo-L-leucines

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ABSTRACT: Oligo(Leu)s containing an oligo(Aib) segment at their C terminus, Boc-Leu$_m$-Aib$_n$-OBzl (m = 4, n = 1, **1**; m = 4, 7, and 10, n = 3, **2–4**; m = 4, 7, n = 5, **5** and **6**), were prepared to investigate the helix-promoting ability of the C-terminal oligo(Aib) segments for oligo(Leu)s. It has been shown that peptides **2–6** have excellent solubility in various organic solvents. From conformational studies by IR absorption spectroscopy, it has been suggested that peptides **2–6** have a helical structure in dichloromethane solution. It has also been indicated from the CD spectra in MeOH that peptides **3**, **4**, and **6** have a helical structure in the solvent. From conformational analyses of IR absorption spectra for their solid samples obtained by slow evaporation of the solvent from dichloromethane solution, it has been indicated that peptides **2–6** have little or no contribution of a β-sheet structure and a large contribution of intramolecularly hydrogen-bonded structures, probably with a large contribution of a helical structure, in the solid state. It is in contrast that peptide **1** and oligo(Leu)s (Boc-Leu$_n$-OBzl, n = 4–6 and 9; **7–10**) have a β-sheet structure in the solid state. These results indicate that the oligo(Aib) segments have a helix-promoting ability toward the N-terminal direction. From conformational studies by IR absorption spectra for the solid samples of peptides **2–6** obtained by slow evaporation of solvent from MeOH solution, it has been indicated that the helical structure of the peptides is relatively unstable in MeOH compared to that in dichloromethane and that only the peptides equal to or larger than dodecapeptide have a stable helical structure in concentrated MeOH solution. This result suggests that the oligo(Aib) segments promote helical folding through preventing the β-sheet construction of the neighboring oligo(Leu) segment.

Regardless[1] of the predicted secondary structure of oligopeptides to be a helical structure, oligopeptides usually have a β-sheet structure[2,3] because of a relatively large critical size of peptides for the development of a stable helical structure in the solid state. The critical size is assumed to be at an eicosapeptide level.[4,5] The β-sheet structure causes insolubility of peptides equal to or larger than an octa- or nonapeptide in most organic solvents and prevents further elongation of the peptide chain.[2,3,6–11] If the construction of the β-sheet structure is prevented by any method, peptide chain elongation would be carried out without an insolubility problem, and conformational transition from an unordered to a helical structure would be observed during peptide chain elongation.

It has been well-known that Aib residues promote helicity and solubility in peptides.[2,9–20] Replacement of some amino acid residues with Aib residues in a peptide sequence has been used to stabilize a helical structure of the peptide.[21] The ability of the Aib residue to promote helical folding in oligopeptides is due to the restriction[12] of the values of the backbone dihedral angles ϕ and ψ of the Aib residue to the narrow region of conformational map which includes helical structures. NMR studies of oligo(Leu)s containing an Aib residue have indicated that one Aib residue initiates helical folding in oligo(Leu)s toward the C-terminal direction from the Aib residue.[22] It was also indicated that the helical promoting ability of the Aib residue toward the N-terminal direction is rather weak. It is expected that an oligo(Aib) segment has a stronger helix-promoting ability than one Aib residue. It has been known that oligo(Aib)s have a stable 3_{10} helix due to the restriction of the values of the backbone dihedral angles ϕ and ψ of the Aib residue, although the stability of the helix depends on the peptide chain length.[18,19] To design and synthesize a peptide in a helical structure, it is desirable for the peptide sequence to have a helix-promoting segment at the C terminus because peptides are usually synthesized from the C terminal to the N-terminal direction. This paper investigates the helix-promoting ability of oligo(Aib) segments at the C terminus of oligo(Leu)s. Oligo(Leu)s containing an oligo(Aib) segment at their C terminus, Boc-Leu$_m$-Aib$_n$-OBzl (m = 4, n = 1, **1**; m = 4, 7, and 10, n = 3, **2–4**; m = 4, 7, n = 5, **5** and **6**), are prepared, and their conformations are investigated.

Experimental Section

General procedures for peptide synthesis were described in a previous paper.[9] The coupling reaction of Boc-Leu-Aib$_{n-1}$-OH with H-Aib-OBzl was carried out by a method described in the literature.[20] The uncorrected capillary melting points are reported. The amino acid compositions of acid hydrolysates were determined with a Shimadzu HPLC LC-3A all amino acid analysis system. The acid hydrolyses of the peptides were carried out with propionic acid/12 M HCl (volume ratio, 2/1) for 2 days at 110 °C. The IR spectra of the peptides in the solid state were recorded

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