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A FIRST EXAMPLE OF CONJUGATED IONIC POLYMER FROM ACETYLENIC SULPHONIUM SALT: POLY(DIMETHYLPROP-2-YNYLSULPHONIUM BROMIDE)

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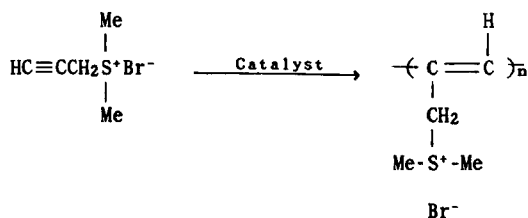
ABSTRACT

Novel conjugated phosphonium salt polymer from dimethyl prop-2-ynylsulphonium bromide was prepared by using various transition metal catalysts. The polymerization was proceeded well to give a moderate yield of polymer. Palladium, platinum, and ruthenium chlorides were found more effective for the polymerization of acetylenic sulphonium salt than those of Mo- and W-based catalysts. The resulting polymers were brown or black powder. The instrumental analyses indicated that the polymer have a conjugated backbone structure carrying the methylene dimethylsulphonium bromide substituent.

INTRODUCTION

In recent years considerable effort has been directed to the synthesis of novel conjugated polymers because of a variety of functions such as electrical conductivity^{1,2}, gas and liquid mixture separation^{3,4}, radiation degradation^{5,6}, and polyelectrolytes⁷. It has been known that

sulfur-containing polymers exhibit moderate hydrophilicity, complex-forming properties, chemical reactivity in hydrolysis and oxidation, and so on⁸. To our knowledge, an example of polyacetylene derivatives having sulfur atom have been virtually restricted to a few cases such as poly(3-thienylacetylene)⁹ and poly[1-(n-alkylthio)-1-propyne]¹⁰. We have also studied the polymerization of mono- and di-acetylenic monomers having sulfur atom and the characterization of resulting polymers¹¹⁻¹³. However there have been no reports on the polymerization of acetylenic sulphonium salts. This paper deals with the polymerization of dimethylprop-2-ynylsulphonium bromide (DPSB) as a first example of conjugated sulphonium salt polymer and the characterization of the resulting poly(DPSB).



Polymerization of DPSB

EXPERIMENTAL

Materials. Propargyl bromide (Aldrich Chemicals, 80wt% solution in toluene) and methylsulfide (Aldrich Chemicals, 99+%) were dried and fractionally distilled. PdCl₂ (Aldrich Chemicals, 99.995%), PtCl₂ (Strem), and RuCl₃ (Aldrich Chemicals) were used as received. MoCl₅ and WCl₆ (Aldrich Chemicals., resublimed, 99+%) and EtAlCl₂ (Aldrich Chemicals, 1.8M solution in toluene) were used as 0.1 or 0.2 M chlorobenzene solution. All polymerization solvents were analytical grade materials. They were dried with appropriate drying agents and fractionally distilled.

Preparation of DPSB. DPSB was prepared by the reaction of propargyl bromide and methylsulfide in acetonitrile as reported method¹⁴ (yield 85%). DPSB was purified by the recrystallization from ethanol-ether. m.p.=110~112°C (lit.¹⁴=112.5~113.5°C). ¹H-NMR (δ, ppm, DMSO-d₆): 4.05, 4.32, 6.01; IR (wavenumbers, cm⁻¹): 3188 (=C-H stretching), 2116 (C=C stretching).

Polymerization of DPSB. A polymerization ampule equipped with rubber septum was flushed with dry nitrogen. Injections of solvent and catalyst solution were done by means of hypodermic syringes from which air and moisture were carefully excluded. A typical polymerization procedure of salt monomer is as follows. Into a 20ml ampule, DPSB (0.5g, 2.76 mmol), PdCl₂ (16.31mg, 0.092mmol), and DMF (5.02mL, [M]₀=0.5M) were added in that order given, and sealed with rubber septum after flushing with nitrogen. After standing at 90 °C for 24hrs, 10ml of ethanol was added to the ampule. This polymer solution was precipitated into an excess ether, filtered from the solution, and then dried under vacuum at 40°C for 24 hrs to give a black powder. The polymer yield was calculated by gravimetry.

RESULTS and DISCUSSION

The polymerization of DPSB was carried out by various transition metal catalysts as shown in Table 1. The polymerization of DPSB by classical palladium, platinum, and ruthenium chlorides was proceeded well to give a moderate yield of polymer. In the polymerization of DPSB by PdCl₂, the polymer yield generally decreased as the monomer to catalyst mole ratio (M/C) increased. The polymerization was also proceeded at the solvents of DMSO, pyridine, and nitrobenzene as like with DMF. PtCl₂ and RuCl₃ also polymerized DPSB to give 36~37% yield. Mo- and W-based catalysts, which have been found to be effective for the polymerization of acetylene derivatives such as 2-ethynylthiophene¹¹, 2-ethynylpyridine¹⁵, propargyl bromide¹⁶, and dipropargyldihexammonium bromide.⁷ However the polymer yield was generally lower than those when palladium, platinum, and ruthenium chlorides are used. MoCl₅ and WCl₆ alone failed to polymerize DPSB. However when EtAlCl₂ cocatalyst was used, a low yield of polymer was obtained.

Figure 1 shows the IR spectra of DPSB and poly(DPSB) prepared by PdCl₂. IR spectrum of polymer showed neither the acetylenic ≡C-H stretching (3188cm⁻¹) nor the C≡C triple bond stretching (2116 cm⁻¹) observed in the IR spectrum of monomer. Instead the C=C double bond stretching of polymer backbone was newly observed at about 1624cm⁻¹. The magic angle spinning, cross-polarization ¹³C-NMR spectrum (Figure 2) of poly(DPSB) showed two peaks. The chemical shift at about 133ppm is due to the carbons on the conjugated double bond, and the methyl and methylene carbon peaks were observed at 37 ppm and 70 ppm, respectively. These instrumental analyses indicated that the poly(DPSB) have a conjugated backbone structure carrying the methylene dimethylsulphonium bromide substituent.

Table 1 Polymerization of Dimethylprop-2-ynylsulphonium Bromide by Transition Metal Catalysts^a

Exp.No	Catalyst System ^b (mole ratio)	M/C ^b	[M] ₀ ^d	Solvent	Polymer Yield (%)
1	PdCl ₂	30	0.5	DMF	51
2	PdCl ₂	50	0.5	DMF	42
3	PdCl ₂	100	0.5	DMF	17
4	PdCl ₂	30	0.5	DMSO	62
5	PdCl ₂	30	0.5	Pyridine	49
6	PdCl ₂	30	0.5	HCO ₂ H	44
7	PdCl ₂	30	0.5	Nitrobenzene	45
8	PtCl ₂	30	0.5	DMF	36
9	RuCl ₃	30	0.5	DMF	37
10	MoCl ₅	30	1.0	Chlorobenzene	0
11	MoCl ₅ -Ph ₄ Sn(1:1)	30	1.0	Chlorobenzene	0
12	MoCl ₅ -EtAlCl ₂ (1:2)	30	1.0	Chlorobenzene	19
13	WCl ₆	30	1.0	Chlorobenzene	0
14	WCl ₆ -EtAlCl ₂ (1:2)	30	1.0	Chlorobenzene	21

^aPolymerization was carried out at 90 °C for 24hrs.

^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min before use.

^cMonomer to catalyst mole ratio.

^dInitial monomer concentration (M).

The TGA thermogram of poly(DPSB) indicated that two major weight losses occur at the temperatures of about 100 and 250°C. The first weight loss at about 100°C corresponds to the absorbed moisture and/or organic residues in the polymers. The second weight loss at about 250°C is due to the elimination of dimethylsulfide and hydrogen bromide, yielding double bond moiety in the polymer.^{17,18} Because the peaks in X-ray diffraction patterns of polymers are all broad and the ratio of half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35,¹⁹ the present conjugated sulphonium polymer is amorphous. The resulting poly(DPSB) were mostly insoluble in organic solvents, regardless of the catalysts used and the polymerization conditions. The insolubility may be originated from the cross-linking of polymer by the activated methylene protons. The color of

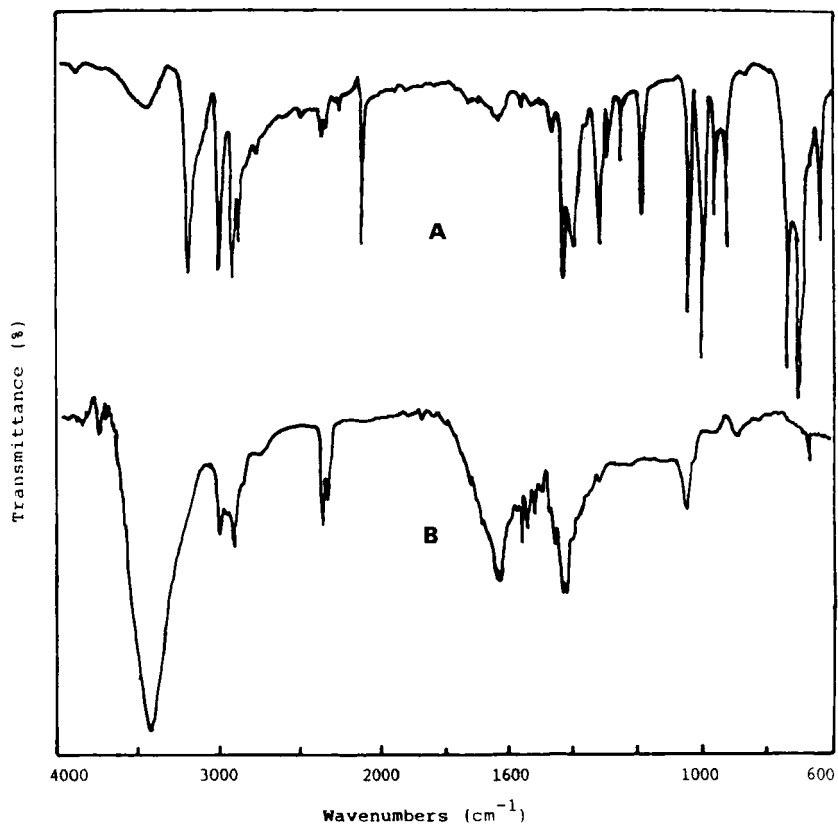


Figure 1 FT-IR spectra of DPSB [A] and poly(DPSB) [B] in KBr pellet.

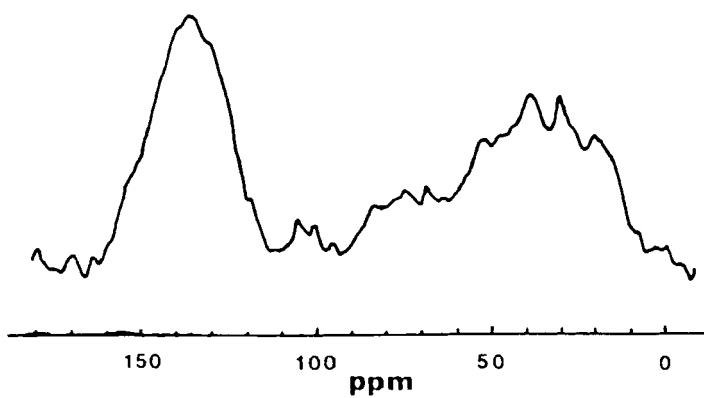


Figure 2 ¹³C-magic angle spinning-cross polarization NMR spectrum of poly(DPSB).

polymers prepared by PdCl_2 and PtCl_2 were mostly black. On the other hand, the polymer prepared by MoCl_5 - EtAlCl_2 was brown color.

The further works on the synthesis of soluble derivatives and the electrophysical properties of the resulting polymer are in progress.

REFERENCES

1. P. Cukor, J. I. Krugler, and M. I. Rubner, Makromol. Chem., **182**, 165 (1981).
2. Y. S. Gal, B. Jung, and S. K. Choi, J. Appl. Polym. Sci., **42**, 1793 (1991).
3. B-Z. Tang, T. Masuda, and T. Higashimura, J. Polym. Sci. Polym. Chem. Ed., **27**, 1261 (1989).
4. Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, J. Appl. Polym. Sci., **43**, 1227 (1991).
5. B-Z. Tang, T. Masuda, T. Higashimura, and H. Yamaoka, J. Polym. Sci. Polym. Chem. Ed., **27**, 1197 (1989).
6. Y. Mujie, Z. Jian, L. Aibing, S. Zhiquan, Z. Mingjian, and L. Senhao, Ibid., **27**, 3829 (1989).
7. K. L. Kang, H. N. Cho, K. Y. Choi, and S. K. Choi, Macromolecules, **26**, 4539 (1993).
8. K. J. Tsuda, J. Adhes. Soc. Jpn., **24**, 200 (1989).
9. S. Tanaka, K. Okuhara, and K. Kaeriyama, Makromol. Chem., **187**, 2793 (1986).
10. T. Masuda, T. Matsumoto, T. Yoshimura, and T. Higashimura, Macromolecules, **23**, 4202 (1990).
11. Y. S. Gal, H. N. Cho, and S. K. Choi, J. Polym. Sci. Polym. Chem. Ed., **24**, 2021 (1986).
12. Y. S. Gal and S. K. Choi, J. Polym. Sci. Polym. Lett. Ed., **26**, 115 (1988).
13. Y. S. Gal and S. K. Choi, J. Polym. Sci. Polym. Chem. Ed., **31**, 345 (1993).
14. G. D. Appleyard and C. J. M. Stirling, J. Chem. Soc. (C), 1904 (1969).
15. Y. S. Gal, H. N. Cho, S. K. Kwon, and S. K. Choi, Polymer (Korea), **12**, 30 (1988).
16. W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, Ibid., **12**, 720 (1988).
17. H. K. Shim, S. K. Kim, J. I. Jin, K. H. Kim, and Y. W. Park, Bull. Korean Chem. Soc., **11**, 11 (1990).
18. J. I. Jin, S. H. Yu, and H. K. Shim, J. Polym. Sci. Polym. Phys. Ed., **31**, 87 (1993).
19. T. Masuda and T. Higashimura, Acc. Chem. Res., **17**, 51 (1984).