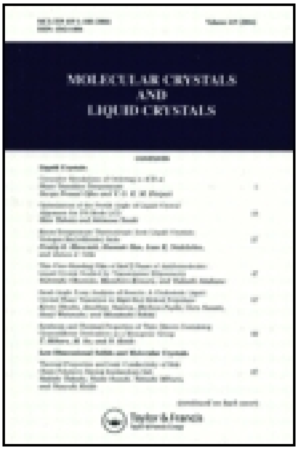

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Synthesis and Properties of Poly(2-Methoxy-5-Propagyl-Oxy-1,4-Phenylenevinylene)

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SYNTHESIS AND PROPERTIES OF POLY(2-METHOXY-5-PROPAGYLOXY-1,4-PHENYLENEVINYLENE)

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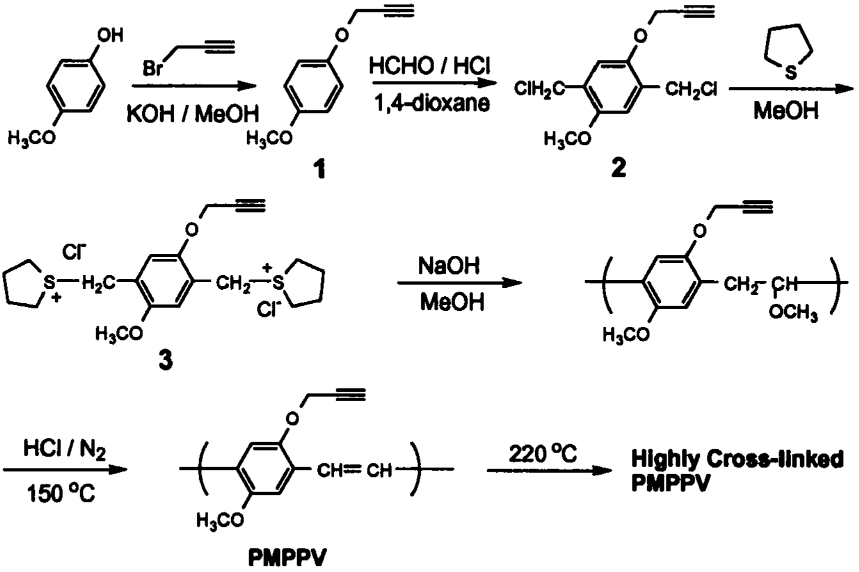
Abstract New PPV derivatives containing cross-linkable acetylene groups, poly(2-methoxy-5-propagyloxy-1,4-phenylenevinylene) (PMPPV) and its PPV copolymers were synthesized through the soluble precursor polymers. PMPPV film was higly cross-linked and lost its properties of a conjugated polymer at over 200 °C. The electrical conductivities of PMPPV films were measured by four probe method after $FeCl_3$ doping. The undrawn and 10 times drawn PMPPV films showed thier electrical conductivities of 1.5 x 10^{-1} and 92 S/cm, respectively. Conjugation length of poly(PV-co-MPPV) was controlled by changing the PMPPV monomer feed ratio.

INTRODUCTION

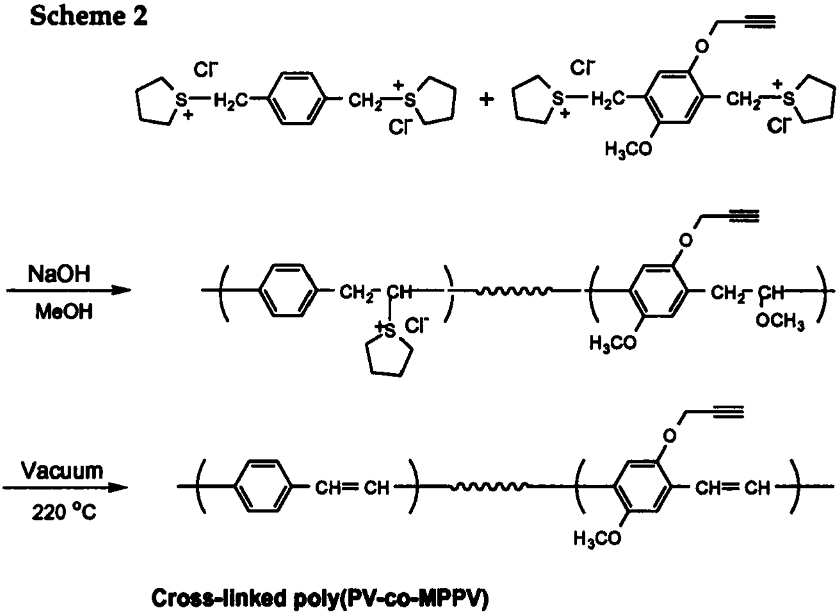
Conjugated polymers are currently attracting much interests as materials for a wide variety of applications including lightweight batteries, electronic and nonlinear optical (NLO) devices.[1] Especially, interests in poly(1,4-phenylenevinylene) (PPV) and its derivatives have been spawned in recent years by the recognition that these polymers reveal high electrical conductivities after doping, high second- and third-order optical nonlinearity, good processibility and high film quality, etc.[2] Also the photoluminescence and electroluminescence of these polymers have been extensively studied for the realization of light-emitting devices and large area multicolor display.[3]

In this article, we report the synthesis and properties of new PPV derivatives containing cross-linkable acetylene groups, poly(2-methoxy-5-propagyloxy-1,4-phenylenevinylene) (PMPPV) and PPV copolymers through a soluble precursor route. The synthetic routes and polymer structures are shown below;

Scheme 1



Scheme 2



Polymerization of PMPPV and Poly(PV-co-MPPV)

We carried out the polymerization in methanol solvent to obtain the organic-soluble precursor polymer because PMPPV precursor polymer was unstabel in water. The salt monomer 3 (2 g, 4.6 mmol) was dissolved in 4.6 mL of methanol (1.0 N) and then, the solution was cooled to 0 °C. The cold equimolar alcoholic NaOH solution (1.0 N) was added to the monomer solution. Soon, highly viscous gum was formed and this was completely dissolved with 20 mL of methanol and then, the precursor polymer solution was stirred at room temperature for 24 h. After stirring for several hours, the viscosity of the precursor polymer solution was disappeared, and the greenish colored organic-soluble precursor polymer was precipitated. This organic-soluble precursor polymer was soluble in dichloromethane, chloroform and other organic solvents. The precursor polymer film of PMPPV was obtained by casting the precursor polymer solution in dichloromethane. The precursor polymer film was flexible and showed good film quality. This organic-soluble precursor polymer film was completely eliminated by introducing a small amount of nitrogen containing HCl gas at 150 °C. This protonic acid catalyzed elimination process for the organic-soluble precursor polymers was reported by Murata et al.[4] For the poly(PV-co-MPPV) copolymers, the total moles of the two monomers were kept constant, but their mole ratios were varied.

RESULTS AND DISCUSSION

The organic-soluble precursor polymer films of PMPPV are soluble in dichloromethane, dichloroethane, THF and trichlorobenzene etc. and showed good film quality. At first, we eliminated these films through conventional thermal elimination conditions i,e at 220 °C for 10 h under vacuum. After elimination reaction, we obtained dark-brown polymer films. Abnormally, these films didn't show the characteristic properties which shown in other eliminated PPV derivatives, such as the strong UV absorption band by π-π^* transitions of conjugated main chain[11] and the characteristic absorption at 960 cm^{-1} in IR spectra which corresponds to the out-of-plane bending mode of the trans-vinylene groups.[5] From these results, we suggested that the acetylene groups and generated double bonds were cross-linked each other during elimination reaction. We found that the cross-linking reaction occurs over 200 °C. When the elimination reaction was performed below 150 °C by flowing HCl gas and nitrogen, we could obtain fully conjugated PMPPV films.

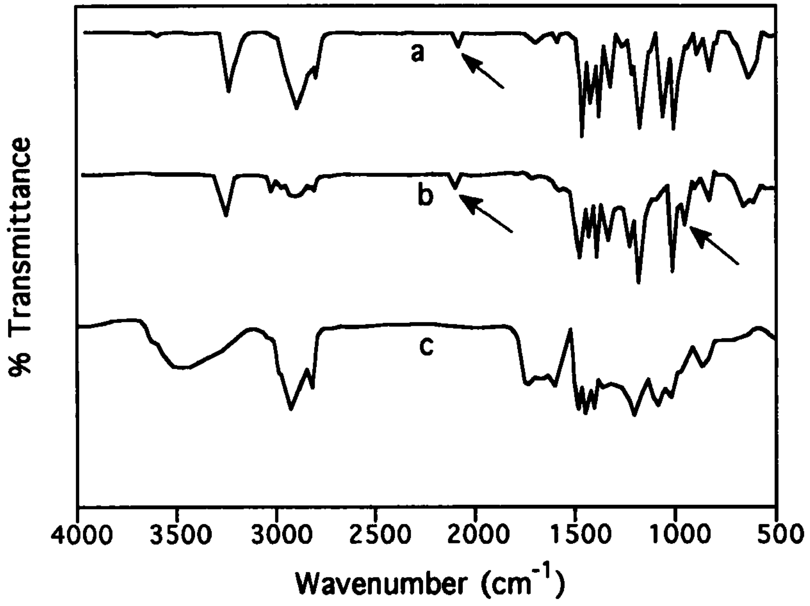


FIGURE 1. FT-IR spectra of (a) organic-soluble precursor polymer (b) PMPPV and (c) cross-linked PMPPV

Figure 1 shows FT-IR spectra of the organic-soluble precursor polymer film of PMPPV (a) the fully conjugated polymer film (b) which obtained after elimination at 150 °C for 3 h by flowing HCl gas and nitrogen. In spectrum (b), a strong absorption peak appears at 960 cm^{-1} which corresponds to the out-of-plane bending mode of the trans-vinylene group. In spectra 1 (a) and (b), the strong absorption peaks of acetylenic hydrogen appeared at about 3280 cm^{-1} and also the characteristic absorption peaks of acetylene triple bond appeared at 2114 cm^{-1}. Figure 1 (c) shows the FT-IR spectrum of PMPPV film which obtained after elimination at 220 °C for 3 h. In this spectrum, the characteristic absorption peaks of acetylene group and trans vinylene groups completely disappeared. These results indicate that acetylene groups and main chain double bonds reacted at high temperature, so the polymer films were highly cross-linked. In other words, the extended π-conjugated system of PMPPV was completely broken after cross-linking reaction.

Figure 2 shows the UV-visible spectra of PMPPV and cross-linked polymer film. The absorption maximum and band edge of PMPPV are located at about 435 and 580 nm, respectively. After thermal treatment at 220 °C for 3 h, the absorption band of longer wavelength region disappeared, suggesting that the extended π-system was broken by the crosslinking reaction.

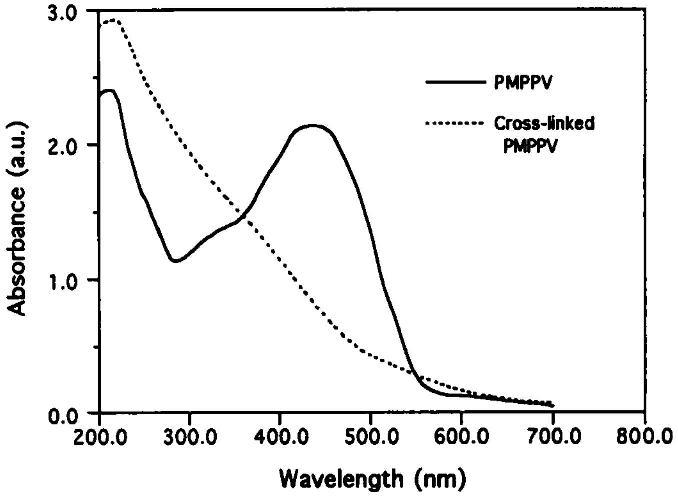


FIGURE 2. UV-visible spectra of PMPPV and cross-linked PMPPV.

Electrical Conductivities of PMPPV films

The electrical conductivities were measured by four probe method after $FeCl_3$ doping. The undrawn and 10 times stretched PMPPV films showed their conductivities of 1.5×10^{-1} and 92 S/cm, respectively. These lower conductivity values of PMPPV mean that a small amount of premature crosslinking might be occured during the elimination reaction because of the acetylene groups of PMPPV polymr. The cross-linked PMPPV films showed no detectable conductivitie, because of the crosslinking of π-conjugated structures.

Conjugation Length Control of Poly(PV-co-MPPV)

From the above results, we found that the conjugated main chains of PMPPV were effectively broken after elimination over 200 °C. We could control the conjugation length of poly(PV-co-MPPV) by varying the MPPV monomer feed ratio. Figure 3 shows the UV-visible spectra of PPV and poly(PV-co-MPPV). In these spectra, the maximum absorptions are gradually shifted moved to the shorter wavelength region by increasing the MPPV monomer feed ratio. 30-Poly(PV-co-MPPV) shows its absorption maximum and edge at 320 nm

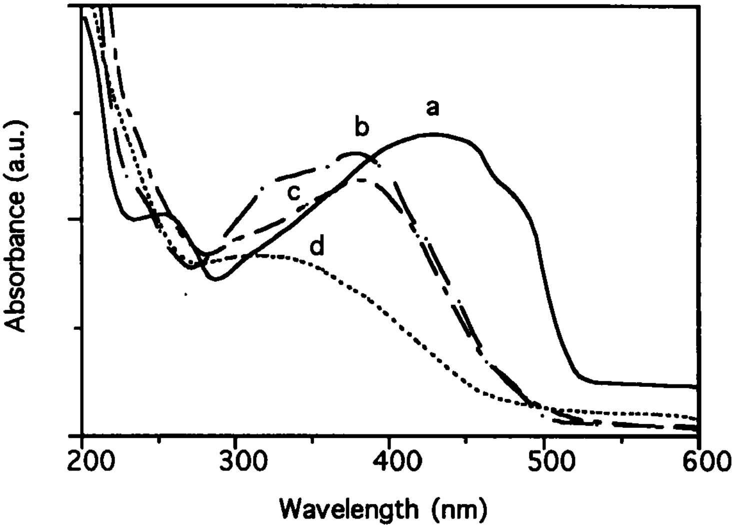


FIGURE 3. UV-visible spectra of (a) PPV, (b) 10-, (c) 20- and (d) 30-poly(PV-co-MPPV) (The numerical values of 10, 20 and 30 stand for the feed mole % of MPPV monomer in comonomer solution)

and 460 nm, respectively. These results are highly blue shifted ones compared with PPV (430 nm/520 nm). These are very important in the area of polymer LEDs, especially in realization of blue color, because we may control the emission colors by controlling the conjugation length of polymers.

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REFERENCES

1. T.A. Skotheim Ed. Handbook of Conducting Polymers (Marcel Dekker, New York, 1986)
2. R.W. Lenz, C.C. Han, J.S. Smith and F.E. Karasz, J. Polym. Sci. Polym. Chem. Ed., 26, 3241 (1988)
3. H. Burroughes, D.D.C. Bradley, A.R. Brown, N. Marks, K. Mackay, R.H. Friend, P.L. Burns and A.B. Holmes, Nature, 347, 539 (1990)
4. H. Murata, S. Tokito, T. Tsutsui and S. Saito, Synth. Met., 36, 95 (1990)
5. D.H. Hwang, J.I. Lee, H.K. Shim, W.Y. Hwang, J.J. Kim and J.I. Jin, Macromolecules, 27, 6000 (1994)