BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 1, pp. 193–200, 1995

0032-3861/95/$10.00+0.00

Synthesis and characterization of poly(2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene) and a series of copolymers containing 1,4-phenylenevinylene units

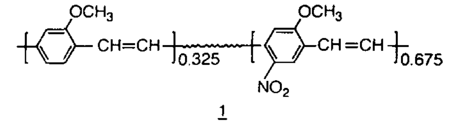
Jung-Il Jin*, Young-Hun Lee and Byung-Ki Nam
Department of Chemistry, College of Sciences, Korea University, 1-Anam Dong,
Seoul 136-701, Korea
(Received 9 May 1994; revised 27 June 1994)

Poly(2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene) (PMNEPV) and a series of copolymers (poly(MNEPV-*co*-PV)) containing varying amounts of 1,4-phenylenevinylene (PV) units have been synthesized via soluble precursor polyelectrolytes. These polymers possess a unique structural feature in which the electron-donating methoxy groups are located on the phenylene rings along the main chain whereas the electron-attracting nitro groups are attached to the side chain styryl substituents. The u.v.-vis. spectra of PMNEPV and the poly(MNEPV-*co*-PV)s revealed two major absorptions arising from π–π^* transitions of the two π-electron systems: the first peak is due to the π-system in the 4-methoxy-4′-nitrostilbene moiety and the second due to the π-system in the backbone. The maximum electrical conductivity of $FeCl_3$- or I_2-doped copolymers increased rapidly initially with the level of MNEPV unit followed by a gradual decrease when the content of MNEPV unit was >7 mol%. The dependence of the electrical conductivity of the present series of copolymers, when doped either with I_2 or $FeCl_3$, is almost the same as that observed earlier by us for poly(2-methoxy-5-(2-phenylethenyl)-1,4-phenylenevinylene) and its copolymers containing the PV unit.

(Keywords: PMNEPV; PPV copolymers; cross-conjugation)

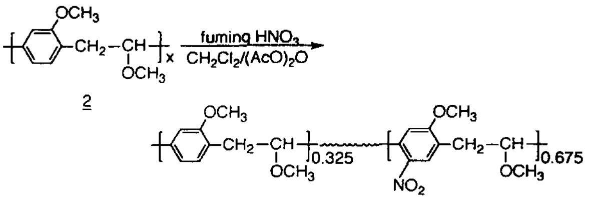
INTRODUCTION

Our previous paper[1] describes a high second-harmonic generation (SHG) ($\chi^{(2)} = 1 \times 10^{-8}$ esu) by a thin poled film of poly(2-methoxy-1,4-phenylenevinylene-*co*-2-methoxy-5-nitro-1,4-phenylenevinylene) (poly(MPV-*co*-MNPV)) (**1**).



1

This polymer was obtained by thermolysis in an electric field of the poled organic-soluble precursor polymer **3** that had been synthesized by nitration of polymer **2**.



2

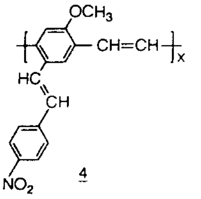
3

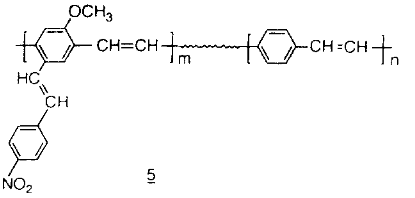
The SHG activity of **1** did not decay for >100 days even when the sample had a thermal history up to 100°C. We believe that this is the first example of an uncrosslinked poly(1,4-phenylenevinylene) (PPV) derivative that exhibits non-relaxing SHG. In contrast, there have been many reports on the stable SHG shown by crosslinked polymers[2–5].

One of the unsatisfactory structural aspects of **1** lies in the fact that the distance between the electron-withdrawing nitro group and the electron-donating methoxy group is relatively small. In order to increase the permanent dipole moment, one has to increase the distance between the electron-donor and electron-acceptor groups. As is well known, the greater the permanent dipole moment of a structural unit with non-linear optical properties, the higher the SHG activity becomes[6–8]. An increased dipole moment could be achieved by inserting a styryl unit between the methoxy and nitro groups as shown in poly(2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene) (PMNEPV) (**4**) and poly(2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene-*co*-1,4-phenylene-vinylene) (poly-(MNEPV-*co*-PV)) (**5**).

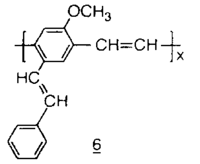
---

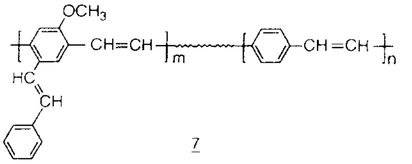
*To whom correspondence should be addressed


4


5

The values of *m* and *n* in **5** indicate the overall composition of the copolymers and not the lengths of each block. Needless to say, poling or alignment of the dipoles is necessary to attain SHG. This paper describes the synthetic details and characterization of **4** and **5** series polymers. Electrical conductivities of the polymers after being doped with I_2 and $FeCl_3$ are also compared with those of poly(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene-vinylene) (PMPEPV) (**6**) and its copolymers containing 1,4-phenylenevinylene units (poly(MPEPV-*co*-PV)) (**7**), whose synthesis and properties were reported by us recently[9].


6


7

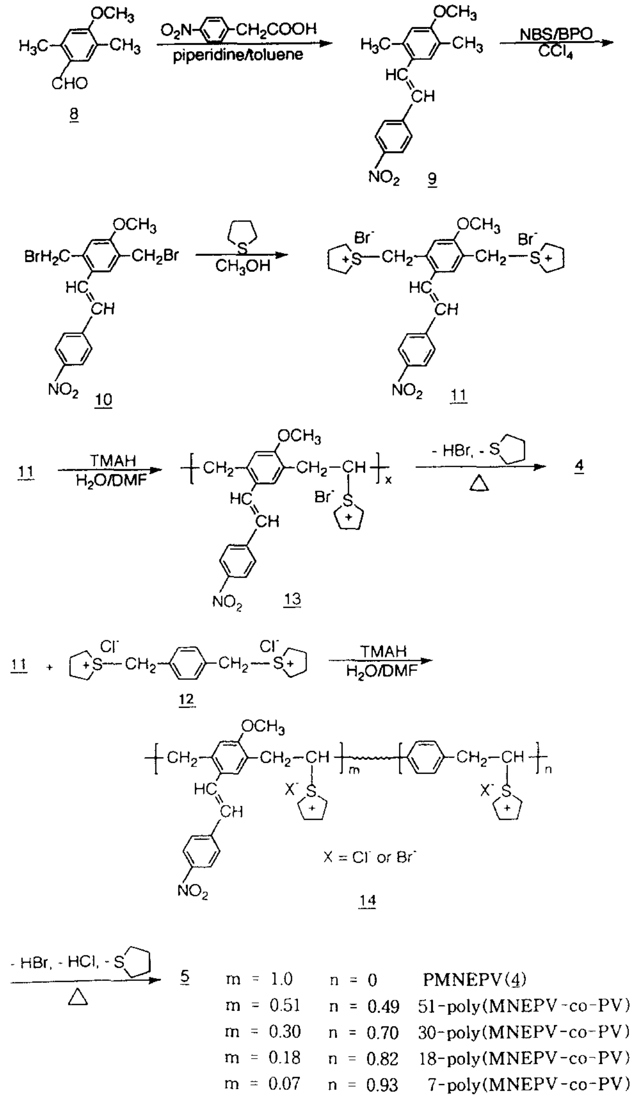
RESULTS AND DISCUSSION

*Synthesis of PMNEPV(4) and poly(MNEPV-*co*-PV)s (5)*

PPV and substituted PPVs can be readily prepared from water- or organic-soluble precursors obtained from base-catalysed polymerization of a bis-sulfonium salt monomer or mixtures of bis-sulfonium salts. This method was orginally described in patents by Wessling and Zimmerman[10], and later Karasz *et al.*[11], Murase *et al.*[12] and Jin *et al.*[13-16] adopted this method for the preparation of many PPV derivatives.

Scheme 1 shows the synthetic routes for preparing PMNEPV and poly(MNEPV-*co*-PV)s. Condensation of 2,5-dimethylanisaldehyde (**8**) and 4-nitrophenylacetic acid in the presence of piperidine produced 4-methoxy-2,5-dimethyl-4′-nitrostilbene (**9**). Benzylic bromation of **9** to **10** was accomplished by the commonly used method using *N*-bromosuccinimide and benzoyl peroxide. Finally, compound **10** was converted to the bis-sulfonium salt monomer **11** by refluxing with excess tetrahydrothiophene. Comonomer **12** is a known salt, and its synthetic method can be found elsewhere[17].

Polymerization of **11** or mixtures of **11** and **12** was carried out at room temperature under a N_2 atmosphere in a mixture of water and *N,N*-dimethylformamide (H_2O:DMF = 1:1 v/v). Addition of DMF to the reaction medium was necessary to keep the polymer formed in solution. Tetramethylammonium hydroxide was used as a catalyst for the polymerization. Polymerization was stopped by neutralizing the reaction mixture to pH 7 with 1 M HCl. From the amount of acid required for neutralization, conversion of the monomer to the polyelectrolyte precursor polymer was calculated. The conversion from **11** to **13**, thus determined, was 75.2%. The monomer conversions for the copolymerizations of mixtures of **11**:**12** = 50:50, 33:67, 20:80 and 10:90 to precursor polymers **14** were 81.5, 84.9, 85.8 and 87.6%, respectively (*Table 1*). After being neutralized, the reaction mixture was subjected to dialysis against distilled water using a tube (Sigma) of molar mass cut-off = 12 000. The dialysed polymers were cast into thin films, which were then subjected to thermolysis at 200°C for 1 h and at 230°C for 5 h to convert to the final polyconjugated polymers **4** and **5**. The films of the final polymers were 10–35 μm thick.



Scheme 1

Properties of precursor polymers

Table 1 summarizes the compositions and solution viscosities of the precursor polymers and the monomer conversions. The polymer yields included in *Table 1* were obtained from the weights of the final polymers prepared by thermolysis of the dialysed precursor polyelectrolytes, i.e. **13** and **14**. The monomer conversion ranges from 75 to 88%, and polymer yields after dialysis were 31–54%. The lower values of PMNEPV are due to the fact that homopolymerization of monomer **11** was concluded in a dilute solution (0.60 g per 50 ml) to prevent precipitation of the polymer formed.

According to the composition data given in *Table 1*, the content of the moiety derived from momomer **11** is

Table 1 Synthetic results and properties of precursor polymers

Polymer[a]	Feed mole ratio 11:12	Actual ratio[b] 11:12	Monomer conversion[c] (%)	Polymer yield[d] (wt%)	η_{inh}[e] (dl g^{-1})
PMNEPV	100:0	100:0	75.2	40.0	0.15
51-Poly(MNEPV-*co*-PV)	50:50	50.7:49.3	81.5	54.3	0.99
30-Poly(MNEPV-*co*-PV)	33:67	29.6:70.4	84.9	41.8	1.80
18-Poly(MNEPV-*co*-PV)	20:80	18.2:81.8	85.8	37.0	2.60
7-Poly(MNEPV-*co*-PV)	10:90	6.9:93.1	87.6	31.0	7.37

[a] The numbers indicate the content (*m*) of MNEPV unit in the final polymer found by elemental analysis
[b] Calculated based on the content of nitrogen determined by elemental analysis (see *Table 2*)
[c] Determined by titration of the reaction mixture
[d] Determined from the weights of the final polyconjugated polymers obtained from the dialysed precursor polymers
[e] Determined at 30°C for 0.2 g dl^{-1} aqueous solutions containing 0.05 M Na_2SO_4

comparable to or slightly lower than that in feed, indicating that the reactivity of monomer **11** is comparable to or slightly less in copolymerization than that of monomer **12**. The solution viscosity of the precursor polymers was measured in the presence of Na_2SO_4 to minimize the artefact arising from the electrostatic repulsion between ionic structures in polyelectrolytes[18]. The solution viscosity decreases rapidly with the content of the MNEPV moiety in the precursor polymer. The viscosity of the copolymer containing 7 mol% MNEPV is 7.37, whereas that of the copolymer containing 51 mol% MNEPV is only 0.99. Also, the value for the PMNEPV precursor polymer is very low. One may simply take this trend as an indication that the actual molecular weight of the copolymers decreases rapidly with the content of the MNEPV moiety. We believe that a direct comparison of the solution viscosity values of the present polyelectrolyte precursors requires special attention with respect to the possible conformational changes in aqueous solution depending on the amount of hydrophobic MNEPV moiety in the copolymers. In other words, the precursor polymer of PMNEPV is expected to be the most hydrophobic in character and to form the tightest coil conformation in aqueous solution leading to the lowest value of the solution viscosity.

On the contrary, the precursor copolymer of 7-poly(MNEPV-*co*-PV) is the most hydrophilic and forms the most expanded coil conformation in aqueous solution resulting in the highest solution viscosity value. Moreover, one has to note that we have collected, using the dialysis method, only the portion whose molar mass is > 12 000. Further evidence to support our supposition are the higher polymer yields for the compositions containing higher levels of the MNEPV moiety. The low values of monomer conversion, polymer yield and solution viscosity for the precursor polymer **13** of PMNEPV are partly due to the fact that homopolymerization had to be conducted at higher dilution for the reason explained above. In short, we believe that the values of the solution viscosity do not directly reflect the molecular weights of the present polymers. We[9] have previously observed the same phenomenon for the solution viscosity of the precursor polymers of **6** and **7**.

Thermal behaviour of the precursor polymers was studied by d.s.c. and thermogravimetric analysis (t.g.a.). Representative d.s.c. and t.g.a. thermograms are given in *Figure 1* for the precursors of PMNEPV (**13**) and 30-poly(MNEPV-*co*-PV) (**14**). Initial endothermic weight loss at ~80–120°C is due to the evaporation of adsorbed water and the second endothermic weight loss at ~125–200°C is caused by the thermolysis reaction to the final polyconjugated polymers accompanied by the loss of HX (X = Br or Cl) and tetrahydrothiophene. The d.s.c. thermograms indicate that thermal degradation starts at ~330°C. In the present investigation, thermolysis of the precursor polymers to the final polymers was performed under vacuum (1.33×10^{-2} Pa) at 230°C for 5 h.

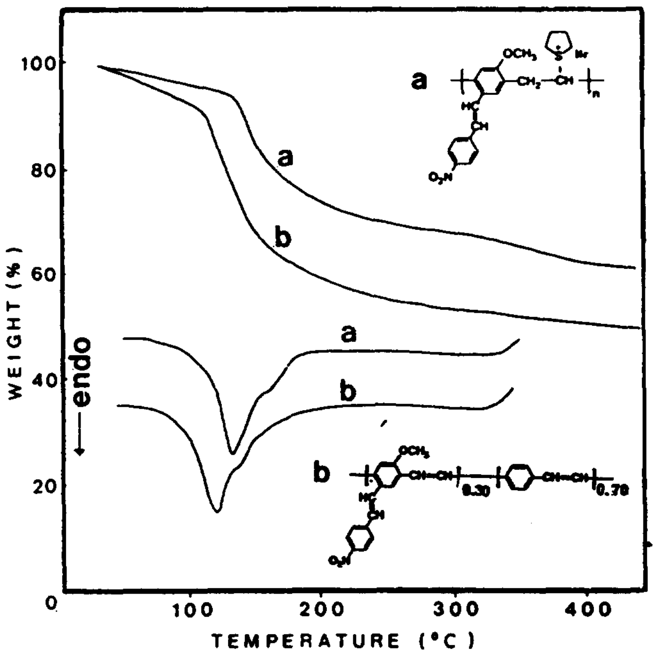


Figure 1 D.s.c. and t.g.a. thermograms of precursor polymer of (a) PMNEPV and (b) 30-poly(MNEPV-*co*-PV) obtained under a nitrogen atmosphere (heating rate 10°C min^{-1})

The Fourier transform i.r. (*FT*i.r.) and u.v.-vis. spectra of the precursor polymers are shown in *Figures 2* and *3*, respectively. The broad, strong absorption at 3100–3600 cm^{-1} is due to presence of adsorbed water. The characteristic absorption peaks of the NO_2 group appear as a doublet at 1514 and 1341 cm^{-1}. In addition, a sharp peak at 1280 cm^{-1} arising from the C–O stretching mode and another peak at 970 cm^{-1} due to the out-of-plane bending mode of *trans*-vinylene C–H can be easily identified. The u.v.-vis spectrum in *Figure 3* shows that

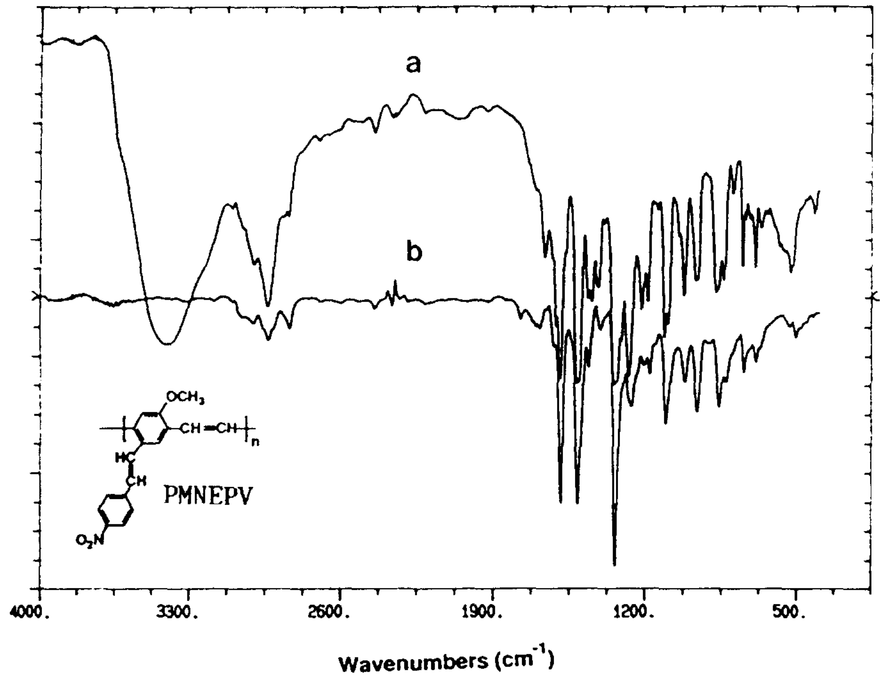


Figure 2 *FT*i.r. spectra of (a) precursor polymer (**13**) of PMNEPV and (b) eliminated PMNEPV (neat film)

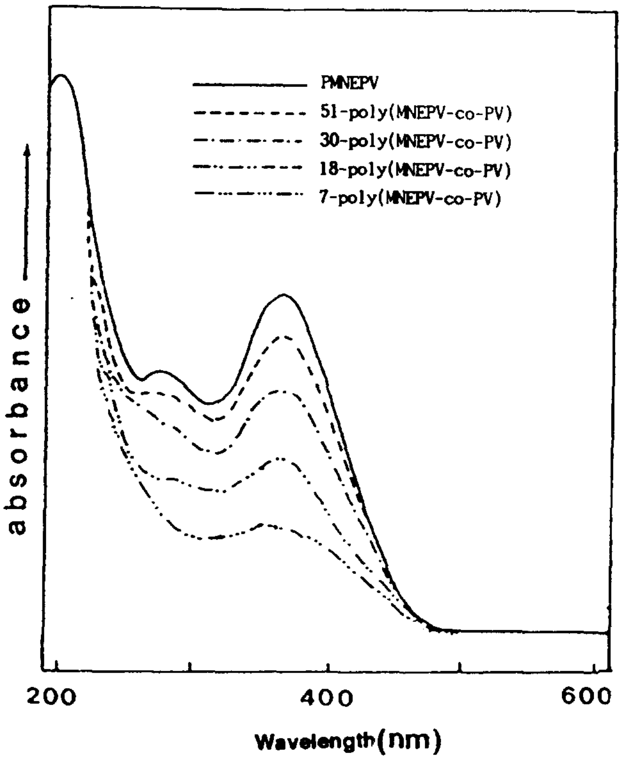


Figure 3 U.v.-vis. spectra of precursor polymers of PMNEPV and poly(MNEPV-*co*-PV)s (neat film on a quartz plate)

the precursor (**13**) of PMNEPV exhibits an absorption at 370 nm due to the π–π^* transition of the 4-methoxy-4′-nitrostilbene structure[19]. As expected, the intensity of this absorption peak decreases with decreasing content of the MNEPV moiety. The additional absorption at 290 nm arises from the substituted nitrobenzene structure[20].

*Structure and properties of PMNEPV and poly(MNEPV-*co*-PV)*

In order to prepare PMNEPV (**4**) and poly(MNEPV-*co*-PV)s (**5**), their corresponding precursor polymers **13** and **14** were subjected to thermolysis under vacuum. The final polymers were obtained as thin films. *Figure 2* compares the *FT*i.r. spectrum of PMNEPV with that of its precursor polymer. The strong absorption at 3100–3600 cm^{-1} disappeared because moisture was removed during thermolysis, whilst the absorption positions due to nitro, ether and *trans*-vinylene groups remained practically unchanged. The peak at ~3000 cm^{-1} arising from the aliphatic C–H stretching mode was weakened significantly due to the elimination of HX (X = Br or Cl) and tetrahydrothiophene by thermolysis.

The u.v.-vis. spectra of the polymers are shown in *Figure 4*. For the sake of comparison, the u.v.-vis. spectrum of PPV prepared separately under the same conditions is included. The maximum position (λ_{max}) of the absorption peak for the π–π^* transition appears at 374 nm for PMNEPV, which is slightly red-shifted from 370 nm for the precursor polymer. The position of λ_{max} of poly(MNEPV-*co*-PV)s apparently gradually shifts to longer wavelength and finally reaches 430 nm for PPV. A close examination of the shape of the absorption peak by PMNEPV around 374 nm, however, implies the coexistence of a smaller, hidden absorption peak whose λ_{max} is located at ~430 nm. *Figure 5* shows the computer-aided resolution of part of the absorption peak of PMNEPV into two separate peaks. Thefefore, it is more reasonable to believe that the peak of PMNEPV in the longest wavelength region is a result of superposition of the original peak (dotted line in *Figure 5*) at 364 nm arising from the π–π^* transition of the 4-methoxy-4′-nitrostilbene moiety with another peak (λ_{max} = 428 nm) (dashed line in *Figure 5*) for the π–π^* transition of the π-electrons along the main chain. One can recognize the existence of another absorption at

288 nm, which is characteristic of the substituted styrene unit. The absorption position of this peak is independent of the composition of the copolymers, but its intensity grows with increasing content of the MNEPV unit in the copolymers.

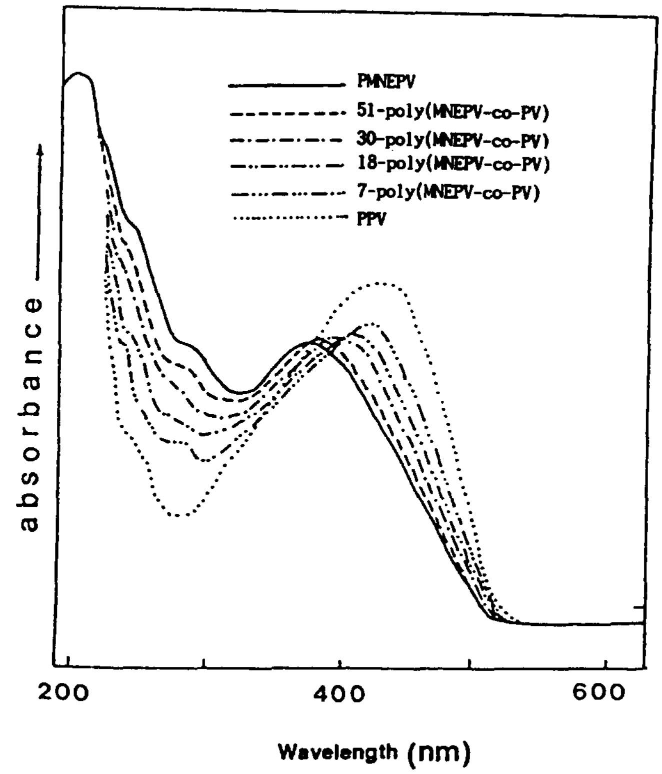
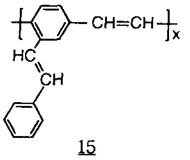


Figure 4 U.v.-vis. spectra of PMNEPV, poly(MNEPV-*co*-PV)s and PPV (neat film on a quartz plate)

Earlier, we[9] clearly observed, for the two related polymers **6** and **15**, poly(2-(2-phenylethenyl)-1,4-phenylenevinylene) (PPEPV), the appearance of two distinctive absorption peaks corresponding to two different π–π^* transitions, i.e. one for the stilbene moiety and the other for the PPV-like structures along the main chain. *Figure 6* compares the u.v.-vis. spectra for the two PPV derivatives **6** and **15** with that of PMNEPV.



15

PPEPV (**15**) reveals two absorptions at 314 and 420 nm, whereas PMPEPV (**6**) shows absorptions at 310 and 435 nm. The peaks in the shorter wavelength region arise from the π–π^* transitions of the stilbene-like structures and the ones in the longest wavelength region from the π–π^* transitions of the π–electrons along the main chains. This indicates that cross-conjugation between the π-systems in the main chain and side chain is insignificant. We also observed the same phenomenon for the copolymers containing the PV unit. Therefore, we can conclude that the absorption positions of the two distinct π–π^* transitions of PMNEPV are not located too far from each other and thus they appear as an overlapped single absorption peak. The same must be true for the absorption characteristics of (poly(MNEPV-*co*-PV)s.

Table 2 summarizes the results of elemental analysis and the maximum conductivities of doped PMNEPV and poly(MNEPV-*co*-PV)s. Based on the nitrogen

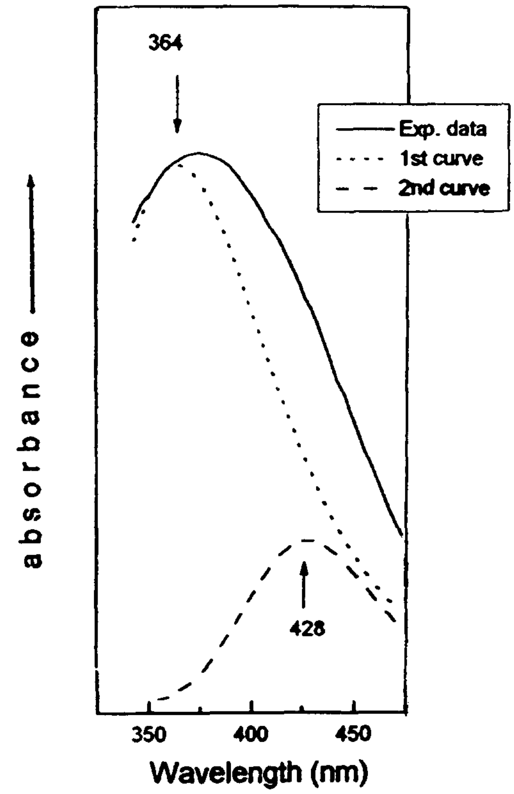


Figure 5 Resolution of the u.v.-vis. spectrum of PMNEPV

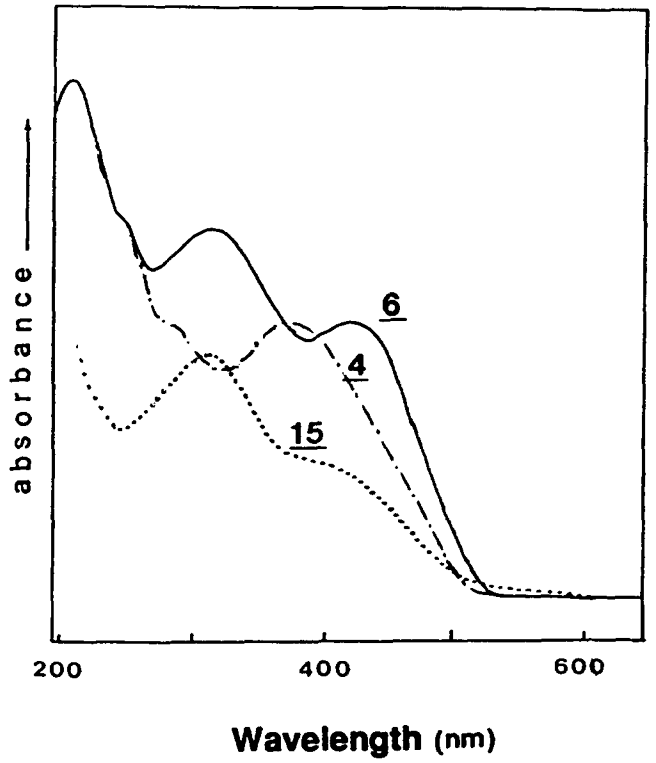


Figure 6 Comparison of u.v.-vis. spectra of polymers **15** (PPEPV), **6** (PMNEPV) and **4** (PMNEPV) (neat film on a quartz plate)

Table 2 Results of elemental analysis and maximum electrical conductivities of PMNEPV and poly(MNEPV-*co*-PV)s

Polymer	Actual composition m:n	Elemental content (wt%)			Maximum conductivity (S cm^{-1})		Degree of doping[a]	
		C	H	N	I_2	$FeCl_3$	I_3^-	$FeCl_4^-$
PMNEPV	100:0	73.14 (73.11)	4.80 (4.70)	4.69 (5.02)[b]	9.4×10^{-6}	7.4×10^{-4}	0.48	0.18
51-Poly(MNEPV-*co*-PV)	50.7:49.3	78.50 (78.61)	4.65 (5.01)	3.70 (3.70)	5.6×10^{-5}	1.7×10^{-3}	0.39	0.12
30-Poly(MNEPV-*co*-PV)	29.6:70.4	83.15 (82.86)	4.94 (5.26)	2.68 (2.68)	2.1×10^{-4}	8.6×10^{-2}	0.27	0.09
18-Poly(MNEPV-*co*-PV)	18.2:81.8	86.38 (86.15)	5.19 (5.46)	1.90 (1.90)	1.6×10^{-3}	0.87	0.22	0.09
7-Poly(MNEPV-*co*-PV)	6.9:93.1	90.37 (90.54)	5.68 (5.71)	0.85 (0.85)	8.6×10^{-3}	8.30	0.22	0.09
PPV	0:100	–	–	–	5.8×10^{-6}	1.7×10^{-5}	0.09	0.02

[a] Dopants were assumed to be present in the form of I_3^- and $FeCl_4^-$

[b] Calculated values in parentheses

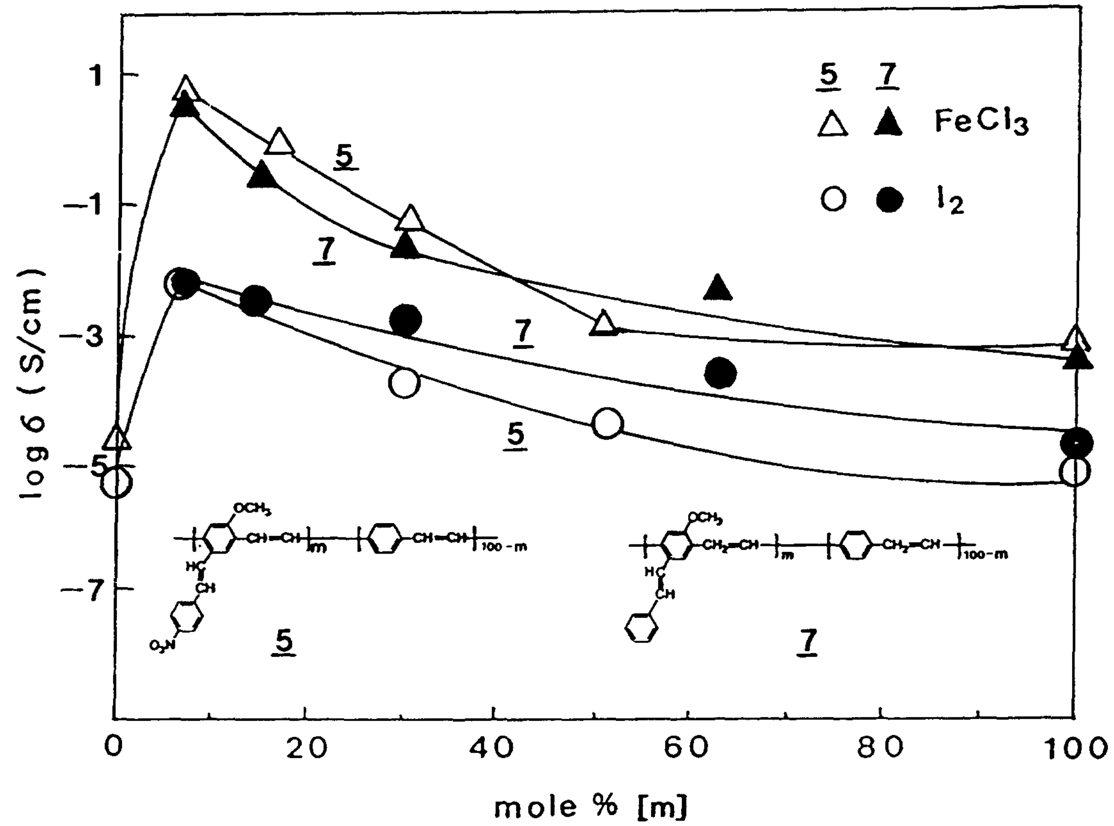


Figure 7 Comparison of the conductivities of I_2- and $FeCl_3$-doped poly(MNEPV-*co*-PV) (**5**) and poly(MNEPV-*co*-PV)s (**7**)

contents found by elemental analysis, we have estimated the actual content of MNEPV unit in the copolymers. The estimated contents of carbon and hydrogen in the copolymers agree very well with the found values. The maximum electrical conductivities of the copolymers were measured by the usual four-in-line probe method after they were doped with I_2 or $FeCl_3$. According to the data given in *Table 2*, the degree of doping steadily increases with the content of MNEPV unit. In contrast, the maximum conductivity initially increases rapidly with the content of MNEPV unit followed by a steady decrease. In other words, a parallelism does not exist between the degree of doping and the maximum conductivity of the doped polymers. The same observations were made earlier by us[9] for PPEPV (**15**), PMPEPV (**6**) and their copolymers.

PPV has electrical conductivities of only 5.8×10^{-6} and 1.7×10^{-5} S cm^{-1}, respectively, for the I_2- and $FeCl_3$-doped polymers with a very low degree of doping for both dopants. However, 7-poly(MNEPV-*co*-PV) reveals much higher conductivities of $\sim 1 \times 10^{-2}$ and 1×10^1 S cm^{-1} when doped with I_2 and $FeCl_3$, respectively.

The degree of doping also increases for both dopants. When the content of MNEPV unit is increased further, the electrical conductivity, however, is lowered although the degree of doping keeps increasing. Finally, the electrical conductivity of PMNEPV reaches a value very close to that of PPV in spite of it having the greatest degree of doping for both I_2 and $FeCl_3$. Consistently higher conductivities are obtained for the $FeCl_3$-doped compositions than the I_2-doped ones, which is expected due to the higher oxidation power of $FeCl_3$.

It is our conjecture that the seemingly anomalous relation between the degree of doping and the electrical conductivity of the present series of polymers is due to the charge-transfer type interaction between the dopant and the side chain styryl unit. Formation of charge-transfer complexes between the two will certainly elevate the apparent degree of doping. At the same time, complexation will simultaneously reduce electrical conductivity due to the conversion of the styryl unit to a more powerful electron withdrawer.

Another very interesting observation is that the electrical conductivities of the present I_2- and $FeCl_3$-doped polymers are almost the same as those[9] of polymers **6** and **7** that do not carry any substituent in the side chain styryl unit. This is shown in *Figure 7*. This phenomenon strongly implies that the nitro group existing on the phenylene ring of the styryl side chain in PMNEPV and poly(MNEPV-*co*-PV)s is hardly influencing the electrical conductivity of the polymers. This can be taken as additional experimental support for the negligible or minor cross-conjugation between the two π-systems in the main and side chains. We believe that such a non-interactive nature of the π-systems in the present polymers can be advantageously utilized in the preparation of polymeric thin films that are expected to exhibit very strong and non-relaxing SHG when the dipolar units of the 4-methoxy-4′-nitrostilbene moiety of the present polymers are properly aligned by poling[21].

EXPERIMENTAL

Synthesis of 2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-phenylene-1,4-dimethylene bis(tetrahydrothiophenium bromide) (11)

4-Methoxy-2,5-dimethyl-4′-nitrostilbene (**9**). 2,5-Dimethylanisaldehyde (**8**; 50.0 g, 0.305 mol) *p*-nitrophenylacetic acid (60.7 g, 0.335 mol) and piperidine (28.5 g, 0.335 mol) were dissolved in toluene (750 ml) in a three-necked, round-bottomed flask, which was equipped with a nitrogen inlet, a mechanical stirrer and a Dean–Stark trap. The mixture was refluxed until the desired amount (5.5 ml) of water was trapped in the Dean–Stark trap. Toluene was removed from the reaction mixture by distillation under reduced pressure. The solid residue was dissolved in methanol (200 ml). Distilled water (50 ml) was added to the solution precipitating out the product. The obtained precipitate was recrystallized from methanol. The product yield was 44.5 g (51.6%), m.p. 119–120°C.

Analysis: calculated for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94%. Found: C, 72.08; H, 6.06; N, 4.80%.

^{1}H n.m.r. ($CDCl_3$) spectrum: δ 7.30–8.30 (m, 6H, aromatic H), 7.07 (s, 1H, vinylene), 6.67 (s, 1H, vinylene), 3.90 (s, 3H, OCH_3), 2.33 ppm (d, 6H, CH_3).

I.r. (KBr) spectrum: 3024 (aromatic C–H stretching), 1507 and 1341 (N–O stretching), 971 cm^{-1} (out-of-plane bending of *trans* vinylene C–H).

2,5-Bis(bromomethyl)-4-methoxy-4′-nitrostilbene (**10**). 4-Methoxy-2,5-dimethyl-4′-nitrostilbene (**9**; 12.0 g, 4.24×10^{-2} mol) prepared above, *N*-bromosuccinimide (16.59 g, 9.32×10^{-2} mol) and benzoyl peroxide (1.20 g, 4.95 mmol) were dissolved in purified CCl_4 (600 ml). The whole mixture was refluxed for 4 h under a nitrogen atmosphere. After the insoluble solid (succinimide) formed was removed by filtration, carbon tetrachloride was removed under reduced pressure. Ethyl acetate (7 ml) was added to the sticky residue precipitating out the crude product. The precipitate was washed further with cold ethyl acetate (15 ml). This compound was used in the next step without any further purification. The product yield was 8.81 g (47.1%), m.p. 224–225°C.

Analysis: calculated for $C_{17}H_{15}Br_2NO_3$: C, 46.29; H, 3.43; N, 3.18%. Found: C, 47.93; H, 3.60; N, 3.23%.

^{1}H n.m.r. ($CDCl_3$) spectrum: δ 7.67 and 8.25 (d, 4H, aromatic H in nitrophenyl structure), 7.68 (s, 1H, aromatic H *ortho* to vinylene), 7.54 and 7.09 (d, 2H, vinylene), 6.87 (s, 1H, aromatic H *ortho* OCH_3), 4.60 (d, 4H, CH_2Br), 3.94 ppm (s, 3H, OCH_3).

I.r. (KBr) spectrum: 3024 (aromatic C–H stretching), 1507 and 1345 (N–P stretching), 1218 (bending of C–Br), 972 (out-of-plane bending of *trans*-vinylene C–H), 684 cm^{-1} (C–Br stretching).

2-Methoxy-5-(2-(4-nitrophenyl)ethenyl)phenylene-1,4-dimethylene bis(tetrahydrothiophenium bromide) (**11**). 2,5-Bis(bromomethyl)-4-methoxy-4′-nitrostilbene (**10**, 6.00 g, 1.36×10^{-2} mol) and tetrahydrothiophene (9.59 g (0.109 mol) were dissolved in methanol (100 ml). The mixture was heated to and maintained at 50°C for 24 h. Methanol and unreacted tetrahydrothiophene were then removed by distillation under a reduced pressure. The residue was mixed with dry cold acetone. The precipitate was thoroughly washed with cold acetone. The product yield was 5.43 g (64.7%).

^{1}H n.m.r. (D_2O) spectrum: δ 7.81 and 8.27 (d, 4H, aromatic H in nitrophenyl), 7.86 (s, 1H, aromatic H *ortho* to vinylene), 7.55 and 7.25 (d, 3H, vinylene and aromatic H *ortho* to OCH_3), 4.80 (s, 2H, benzylic H *ortho* to vinylene), 4.57 (s, 2H, benzylic H *ortho* to OCH_3), 4.00 (s, 3H, OCH_3), 3.47 (m, 8H, thiophenium), 2.29 ppm (m, 8H, CH_2).

I.r. (KBr) spectrum: 2953 (aliphatic C–H stretching), 1515 and 1346 (N–O stretching), 972 cm^{-1} (out-of-plane bending of *trans*-vinylene C–H).

*Preparation of precursor polymers (13 and 14) of PMNEPV and poly(MNEPV-*co*-PV)*

Compound **11** (0.600 g, 0.972 mmol) was dissolved in a mixture of distilled water and *N*,*N*-dimethylformamide (50 ml, 1:1 v/v), through which nitrogen was bubbled for 10 min. Then, 1.06 ml (0.972 mmol) of 0.918 M tetramethylammonium hydroxide was added and the mixture was stirred for 1 h at room temperature under a nitrogen atmosphere. The reaction mixture was titrated to pH 7 using 1 M HCl. The monomer conversion estimated from the amount of 1 M HCl required was 75.2%. The neutralized solution was subjected to dialysis for 3 days against distilled water using a dialysis tube (Sigma) with molecular weight cut-off = 12 000.

In order to prepare the precursor copolymers (**14**), monomer **11** was mixed with comonomer **12**[17] in the mole ratio of 50:50, 33:67, 20:80 and 10:90. For example, 0.400 g (0.648 mmol) of **11** and 0.228 g (0.648 mmol) of **12** were copolymerized in a mixture of H_2O and DMF (10 ml, 1:1 v/v) in the same way as for the preparation of **13**. The monomer conversion was 82%. For the other three copolymerizations, the conversion was 85, 86 and 88%, respectively.

*Preparation of PMNEPV (4) and poly(MNEPV-*co*-PV) (5)*

The dialysed precursor polymers were cast into thin films (10–35 μm thick) directly from the aqueous solution and subjected to thermolysis for 1 h at 200°C and subsequently for 5 h at 230°C under a reduced pressure (1.33×10^{-2} Pa).

Identification and characterization of intermediates and polymers

Elemental analyses were performed by Korea Basic Science Center using a Perkin–Elmer model 240 elemental analyzer. The i.r.- and u.v.-vis. spectra of the compounds and polymers were recorded, respectively, on an Alpha Centauri FTIR (Mattson) instrument and on a Hewlett Packard 8452A spectrophotometer. The thermal properties of the precursor polymers were examined under a nitrogen atmosphere on a d.s.c. instrument (DuPont 910) and a thermogravimetric analyser (Mettler 3000). The heating rate was 10°C $\min^{-1}$. The solution viscosity of the precursor polymers was measured at 30°C for the aqueous solution ($0.2\ g\ dl^{-1}$) containing 0.05 M Na_2SO_4.

Doping and measurement of electrical conductivities of the polymers

The thin polymeric film (10–35 μm thick) were attached to the platinum electrodes in a four-in-line probe chamber. Carbon paste was used for attachment. Doping with I_2 vapour was conducted at a pressure of 0.133 Pa until the films exhibited maximum conductivities. From the weight increase, the degree of doping was estimated. When the dopant was $FeCl_3$, the films were immersed at room temperature into an $FeCl_3$-saturated nitromethane solution. After the surfaces of the doped films were rinsed with fresh nitromethane, the films were attached to the electrodes.

CONCLUSIONS

We have succeeded in synthesizing poly(2-methoxy-5-(2-(4-nitrophenyl)ethenyl)-1,4-phenylenevinylene) (PMNEPV) and a series of copolymers (poly(MNEPV-*co*-PV)) containing the 1,4-phenylenevinylene unit. These polymers show a unique structural feature in which styryl units are attached to the phenylene rings in the PPV-like main chain. Moreover, the main chain phenylene rings carry the electron-donor methoxy groups whereas the phenylene rings in the styryl side chains carry the electron-acceptor nitro groups. These polymers are expected to show stable strong SHG and other second-order non-linear optical properties, if they can be properly poled to align the dipolar units[1,21].

The u.v.-vis. spectra of the polymers reveal two major absorption peaks resulting from π–π^* transitions: one for the π-electrons along the main chain and the other for the π-electrons of the stilbene-like structure. The appearance of two separate absorption peaks indicates that there is very little cross-conjugation between the two π-systems.

The electrical conductivity of I_2- or $FeCl_3$-doped poly(MNEPV-*co*-PV)s increases only up to 7 mol% MNEPV and then gradually decreases with further increase in MNEPV content. On the contrary, the degree of doping steadily increases for both dopants with the content of MNEPV unit. This observation is interpreted in terms of charge-transfer type interactions between the dopants and styryl units. Surprisingly enough, the electrical conductivity of the present copolymers is practically the same as for poly(2-methoxy-5-(2-phenyl)-ethenyl-1,4-phenylenevinylene-*co*-1,4-phenylenevinylene) (7; poly(MPEPV-*co*-PV)). This phenomenon again supports the non-interacting π-electron structures for the present polymers.

ACKNOWLEDGEMENTS

We are grateful to the Korea Science and Engineering Foundation for supporting this research. Y.-H. Lee wishes to express his thanks to the Han-Hwa group for the special post-graduate scholarship.

REFERENCES

1 Jin, J.-I. and Lee, Y.-H. *Mol. Cryst. Liq. Cryst.* 1994, **247**, 67
2 Eich, M., Reck, B., Yoon, D. Y., Wilson, C. G. and Bjorklund, G. C. *J. Appl. Phys.* 1989, **66**, 3241
3 Mandal, B. K., Chen, Y. M., Lee, J. Y., Kumar, J. and Tripathy, S. *Appl. Phys. Lett.* 1991, **58**, 2459
4 Chen, M., Yu, L. P., Kalton, L. R., Shi, Y. Q. and Steier, W. H. *Macromolecules* 1991, **29**, 5741
5 Chen, M., Dalton, L. R., Yu, L. P., Shi, Y. Q. and Steier, W. H. *Macromolecules* 1992, **25**, 4032
6 Williams, D. J. *Angew. Chem. Int. Edn Engl.* 1984, **23**, 690
7 Chemla, D. S. and Zyss, J. (Eds) 'Nonlinear Optical Properties of Organic Molecules and Crystals', Vol. 1, Ac(demic Press, Orlando, 1986, Ch. II-3
8 Prasad, P. N. and Williams, D. J. 'Introduction to Nonlinear Optical Effects in Molecules and Polymers', John Wiley & Sons, New York, 1991
9 Jin, J.-I., Lee, Y.-H., Park, C.-K. and Nam, B.-K. *Macromolecules* 1994, **27**, 5239
10 Wessling, R. A. and Zimmerman, R. G. *US Pat. 3 401 152*, 1968; *US Pat. 3 706 677*, 1972
11 Karasz, F. E., Capistran, J. D., Gagnon, D. R. and Lenz, R. W. *Mol. Cryst. Liq. Cryst.* 1985, **18**, 327
12 Murase, I., Ohnishi, T., Noguchi, T., Hirooka, M. and Murakami, S. *Mol. Cryst. Liq. Cryst.* 1985, **118**, 333
13 Jin, J.-I., Kim, J.-C. and Shim, H.-K. *Macromolecules* 1992, **125**, 5519
14 Jin, J.-I., Park, C.-K. and Shim, H.-K. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 93
15 Jin, J.-I., Park, C.-K. and Shim, H.-K. *Macromolecules* 1993, **26**, 1799
16 Jin, J.-I., Lee, Y.-H. and Shim, H.-K. *Macromolecules* 1993, **26**, 1805
17 Gagnon, D. R., Capistran, J. D., Karasz, F. E., Lenz, R. W. and Antoun, S. *Polymer* 1987, **28**, 567
18 Morawetz, H. 'Macromolecules in Solution', 2nd Edn, John Wiley & Sons, New York, 1975, pp. 344–363
19 Robinson, J. W. (Ed.) 'Handbook of Spectroscopy', Vol. II, CRC Press, Cleveland, 1974, p. 140
20 Stern, E. S. and Timmons, C. J. 'Electronic Absorption Spectroscopy in Organic Chemistry', 3rd Edn, Edward Arnold Ltd, London, 1970, pp. 130–133
21 Hwang, D.-H., Lee, J.-I., Shim, H.-K., Hwang, W.-Y., Kim, J.-J. and Jin, J.-I. *Macromolecules* 1994, **27**, 6000