

# Mechanism Analysis of the PEG-Participated Gilch Synthesis for Soluble Poly(*p*-phenylene vinylene) Derivatives

CHUN YIN, CHANG-ZHENG YANG

Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, People's Republic of China 210093

Received 1 May 2000; accepted 2 October 2000

**ABSTRACT:** By introducing poly(ethylene glycol) (PEG) into the Gilch reaction system for the synthesis of soluble poly(*p*-phenylene vinylene)s (PPVs), significant changes were observed. First, with the involvement of PEG, the polymerization degree increases significantly and the molecular weight distribution becomes wider. The multimodal characteristic of the GPC curves at low conversions is quite evident. Second, at low PEG content, gelation dramatically disappears; with an increase of PEG, gelation reappears. From the above experimental results, the existence of various types of polymerization-active species and the anionic polymerization mechanism are confirmed, which are due to the dissociation of the carbanion–cation pairs by the complexing effect of PEG. At the same time, the enhanced dissociation of the base (*t*-BuO<sup>−</sup> K<sup>+</sup>) ion pairs by PEG may be responsible for the dramatic disappearance of gelation. Free *t*-BuO<sup>−</sup> anions have strengthened the basicity and accelerated the conjugation-formation process which competes with the interchain by-reactions. Gelation is therefore avoided. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 263–268, 2001

**Key words:** soluble poly(*p*-phenylene vinylene) derivatives; Gilch route; gelation; light-emitting; anionic polymerization

## INTRODUCTION

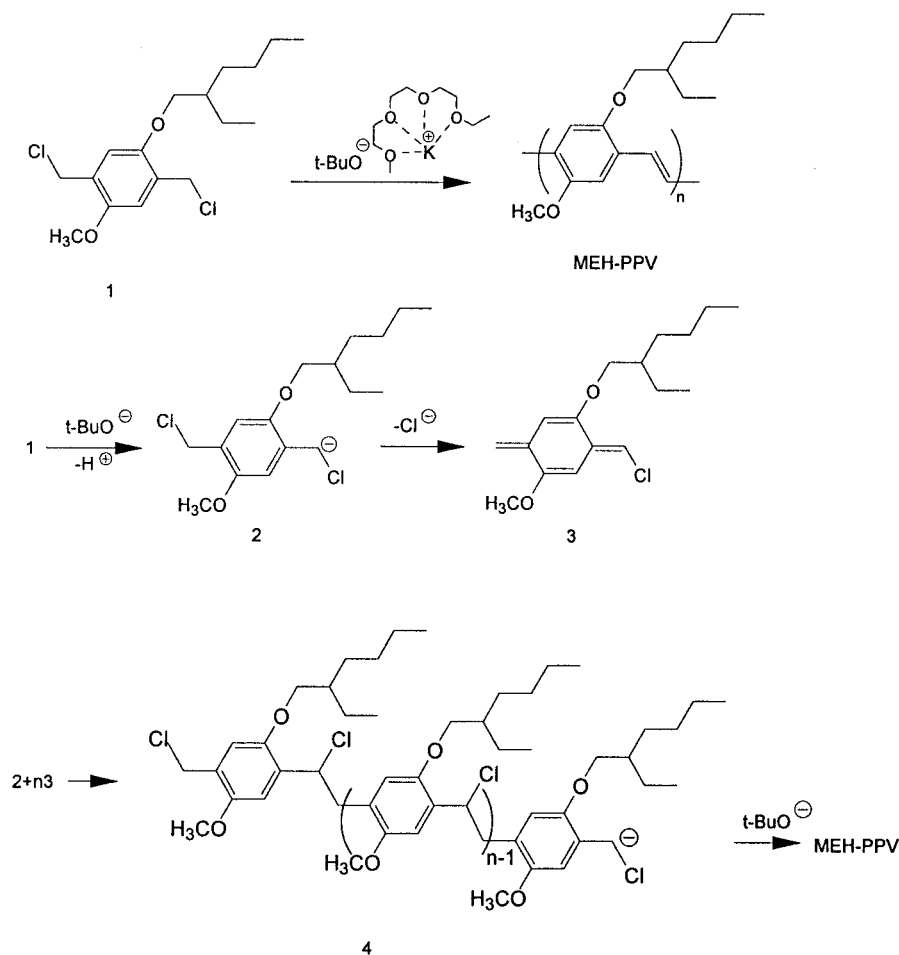
As a famous class of optoelectronic polymers, poly(*p*-phenylene vinylene)s (PPVs) have attracted much attention in recent years.<sup>1,2</sup> In particular, PPVs with a solubilizing side chain linked to the polymer backbone exhibit great advantages in processing, since these soluble conjugated polymers can be cast directly into thin film.<sup>3</sup> They can be used to fabricate flexible light-emitting devices<sup>4</sup> or hybridized easily with other organic or inorganic materials.<sup>5,6</sup> Examples of these soluble PPV derivatives, such as poly[2-(2'-ethylhexyloxy)-5-

methoxy-1,4-phenylene vinylene] (MEH-PPV),<sup>7</sup> poly[2-(2'-ethylhexyl)-5-butyl-1,4-phenyl vinylene] (BuEH-PPV),<sup>8</sup> and poly[2-(2,7-dimethyl octyloxy)-5-methoxy-1,4-phenylene vinylene] (OC<sub>1</sub>C<sub>10</sub>-PPV),<sup>9</sup> were extensively investigated.

Soluble PPVs are widely synthesized through a one-step route, that is, the Gilch route,<sup>10</sup> which shows a greater facility over various precursor routes. In this route, 1,4-bis(halomethyl)benzenes are polymerized in the presence of a base (usually, *t*-BuOK). But the Gilch route usually suffers from a severe gelation problem,<sup>7</sup> which leads to the loss of processibility of the resulting polymer. In addition, the polymerization mechanism has not been fully clarified yet. Both a free-radical and an anionic polymerization mechanism have been proposed, but neither of the two has been sufficiently demonstrated by experimental results.<sup>11,12</sup> If our

Correspondence to: C. Yin (cyin@china.com).  
Contract grant sponsor: National Natural Science Foundation of People's Republic of China.

*Journal of Applied Polymer Science*, Vol. 82, 263–268 (2001)  
© 2001 John Wiley & Sons, Inc.



**Scheme 1** Polymerization process of the Gilch route.

understanding toward the mechanism of the Gilch route can be expanded, it will be very meaningful to help us to improve the quality of these polymers, meeting the demand of high-performance device fabrications. It is noticeable that the Gilch polymerization differs greatly from traditional polymerization: The actual monomer **3** is *in situ* formed from the dehydrochlorination of the added monomer **1** (see Scheme 1). This makes the relation among various intermediates very complicated and results in a great difficulty for investigation of the mechanism. Although several modified Gilch routes have been built up, they are mainly an effort to overcome the gelation problem. Wudl and Srdanov first found that by slow or intermittent addition of a great excess of the base gelation could be minimized.<sup>13</sup> Another gelation-free Gilch route is realized by introducing *tert*-butylbenzyl chloride into the synthetic system.<sup>11</sup> In this article, we introduced poly(ethylene glycol) (PEG), a complexing agent, into the

reaction system. By borrowing the concepts and analytic methods widely applied in the research of traditional anionic polymerization, the changes in the molecular weight distribution and gelation process are discussed.

## EXPERIMENTAL

### Instrumentation

Gel permeation chromatography (GPC) was carried out on a Waters Instruments 590 with a reflective index detector. The oven of the GPC instrument was maintained at 20°C. The GPC eluting solvent was high-grade tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Molecular weight calibrations under these conditions were carried out with polystyrene standards. Infrared measurements were made on a Bruker IFS66V FTIR spectrometer. UV-vis spectra were obtained

**Table I Polymerization Conditions and Results**

Entry	PEG (g)	THF (mL)	$M_w$ ( $\times 10^5$ )	PD ( $M_w/M_n$ )	Reaction Time (min)	% Yield
1	0.5	90	5.08	153	600	59
2	1.0	90	9.27	121	600	57
3	3.0	90	11.9	146	600	54
4	5.0	90	Gelation		600	61
5	1.0	60	10.4	134	600	56
6	1.0	90	9.47	126	5	20
7	1.0	90	6.07	61	10	25

on a Shimadzu UV-3000 spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 240C elemental analyzer.  $^1\text{H-NMR}$  spectra were measured with a Bruker 300-MHz spectrometer.

### Materials

THF was dried by refluxing it with Na, followed by distillation under a nitrogen atmosphere immediately before use. PEG, with an average molecular weight of 1500, was vacuum-dried at 60°C for 48 h immediately before use. *t*-BuOK was purchased from Acros Organics (Belgium) and used as received.

### Preparation of Monomer (1)

1,4-Bis(chloromethyl)-2-methoxy-5-(2-ethyl-hexyloxy)benzene was synthesized as described in the literature.<sup>14</sup>

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.95(s, 2H, Ar—H), 4.62 (s, 4H,  $\text{CH}_2\text{—Cl}$ ), 3.84 (t, 5H,  $\text{—O—CH}_2$ ,  $\text{—O—CH}_3$ ), 0.9–1.5 (m, 15H,  $\text{—C}_7\text{H}_{15}$ ).

ANAL. Calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Cl}_2$ : C, 61.26%; H, 7.86%. Found: C, 61.34%; H, 7.69%.

### Polymerization

A mixed solution of 2.6 g (23 mmol) of *t*-BuOK and 0.5–5 g of PEG in 30 mL THF was added quickly into a solution of monomer **1** (1.0 g, 3 mmol) in 60 mL (or 30 mL) THF under the protection of  $\text{N}_2$  and with mechanical stirring; the reaction temperature was kept at  $30 \pm 2^\circ\text{C}$ . After the polymerization (from 5 to 600 min), 180 mL of methanol was added into the reaction system and stirred for 30 min. The precipitate was then filtered. The obtained orange products were vacuum-dried at room temperature until constant weight. No further reprecipitation was carried out in order to retain the original molecular weight distribution.

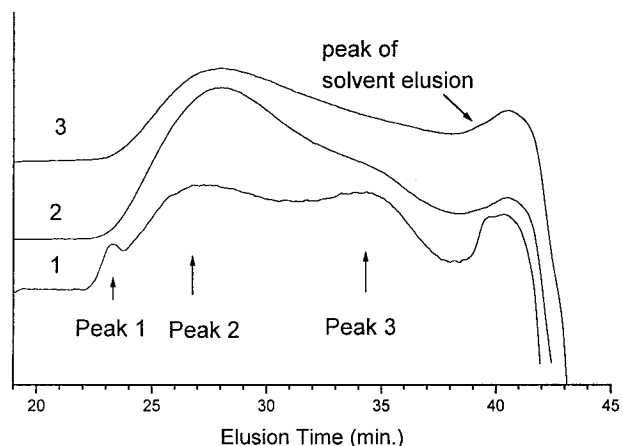
## RESULTS AND DISCUSSION

### Synthesis

MEH-PPV was synthesized at the condition that the base was added all at once. The synthetic results are listed in Table I. All the FTIR spectra of the products are the same as those of MEH-PPV reported previously.<sup>11</sup> The absorption peaks at 3056 and 968  $\text{cm}^{-1}$ , which are due to the olefinic C—H stretch and the *trans*-substituted olefinic C—H bend, respectively, are very evident. The absorption peaks of the UV-vis (THF solution) spectra are at 500 nm. Elemental analysis data show a high purity of these products, typically C, 77.71%, and H, 9.16% (experimental); C, 78.42%, and H, 9.26% (calculated for  $\text{C}_{17}\text{H}_{24}\text{O}_2$ ). These results indicate the conjugated structure of these products.

There are two important features of this PEG-participated Gilch polymerization: First, gelation becomes controllable and is no longer sensitive to the adding mode of *t*-BuOK. In the absence of PEG, if the base is added all at once, the gelation is so severe that almost all the resulting polymer is insoluble. When the PEG content is not high (within 1 g in Table I), the resulting polymer is completely soluble in THF and chloroform. When the PEG content is increased up to 3 g, one can observe an obvious increase of viscosity in the reaction system. The observable viscosity is usually an implication of slight microgelation in the solution (in this case, the polymer solution is apparently uniform, but is not easy to be filtered through 0.5- $\mu\text{m}$  filters).<sup>11</sup> However, when as much as 5 g PEG is used, a sudden gelation occurs within only a few seconds and the resulting polymer is insoluble.

It is evident that at a low PEG content gelation disappears dramatically; with increase of the PEG content, the disappeared gelation reappears.



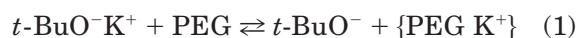
**Figure 1** GPC curves of MEH-PPV obtained at various reaction times: (1) 5 min; (2) 10 min; (3) 600 min (also see Table I).

In fact, when a great excess amount of PEG (e.g., 5 g) is applied, the gelation is much more vigorous than that in the absence of PEG. Second, the molecular weight distributions are especially wide (see Table I). The mass average molecular weight ( $M_w$ ) is usually in the range of  $5 \times 10^5$  to  $10 \times 10^5$ . In comparison, the  $M_w$  of MEH-PPV from the Gilch route reported by Hsieh et al.<sup>11</sup> is  $3.3 \times 10^5$  (maximum), and by Wudl and Srdanov,<sup>13</sup> it is also  $3 \times 10^5$ . The  $M_w$  of OC<sub>1</sub>C<sub>10</sub>-PPV, a soluble PPV derivative which is very similar to MEH-PPV, is  $1.5 \times 10^6$  as reported by Becker et al.,<sup>12</sup> but, noticeably, the conditions are greatly different from other modified Gilch routes. 1,4-

Dioxane is used as a solvent to replace THF, and the reaction temperature is as high as 98°C. Figure 1 shows GPC curves at various reaction times (5, 10, 600 min at 1 g PEG content). With an increased reaction time, these curves change from trimodal to bimodal and monomodal.

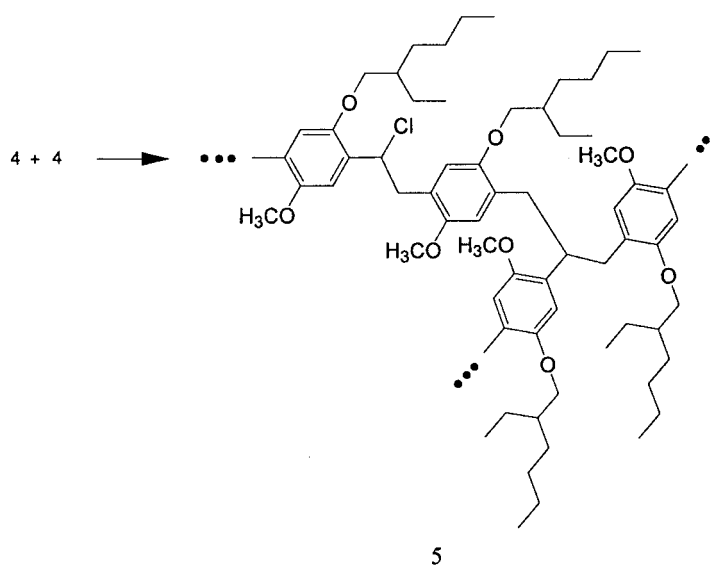
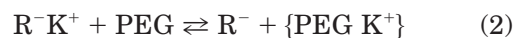
### Complexing Effects of PEG

There are two kinds of ionized organic species in the reaction system, that is,  $t\text{-BuO}^- \text{K}^+$  and  $\text{R}^- \text{K}^+$ , where  $\text{R}^-$  represents various carbanionic intermediates in the reaction system, such as **2**, **4**, and the higher generation macroanions **5** (see Schemes 1 and 2). (Scheme 2) THF is a polar solvent and PEG is a well-known complexing agent. When PEG is added to the reaction system, there will be an additional complexation between PEG and the organic ionic compounds. With respect to  $t\text{-BuOK}$ , the enhanced complexation is shown in (1):



The created free  $t\text{-BuO}^-$  will have enhanced basicity and be advantageous to the elimination process of **1** to **3** and the conjugation-formation process of the precursor polymer **4** to MEH-PPV.

With respect to  $\text{R}^- \text{K}^+$ , there is the following equilibrium according to the achievements in an anionic polymerization study<sup>15,16</sup>:



**Scheme 2** Potential by-reaction in the Gilch polymerization.

where  $R^-K^+$  is the contact ion pair, and  $R^-$ , the dissociated free anion. But it is possible there exists an intermediate between the contact and the completely dissociated ion pairs, which may be the complex consisting of an ion pair and PEG, as shown in (3):



Such complexes widely exist in a conventional anionic polymerization system. In this case, there will be three types of active anionic species in the system. The complex  $\{RK-PEG\}$  is possibly a loose ion pair, which bears enhanced activity compared with contact ion pairs, but its activity is not as high as that of the free anions.

Since the amount of the base is much larger, the existence of a large number of cations will suppress the dissociation of  $R^-K^+$  ion pairs to some extent. On the other hand, *t*-BuOK is more readily dissociated. Therefore, free *t*-BuO<sup>-</sup> should be substantial when compared with free carbanions. However, if excess PEG is added, the amount of free carbanions will increase and have a significant influence on the reaction system.

#### Evidence for the Dissociation of $R^-K^+$ Pairs and the Anionic Polymerization Mechanism of the Gilch Route

A multimodal distribution of molecular weight is a typical phenomenon in traditional anionic polymerization systems, when part of the ion pairs is dissociated to be free ions by solvating or by the addition of some coordinating agents such as amines or ethers. And this is more evident at low conversion. A similar phenomenon was also observed in our experiment. A group of typical GPC curves of the products obtained from various reaction periods is shown in Figure 1. From the trimodal molecular weight distribution in curve 1 (5 min), it is reasoned that there are three types of polymerization-active species in the PEG-participated Gilch system. Peaks 2 and 3 are very strong and wide in curve 1, reflecting that the amounts of two corresponding species are relatively large. According to the achievements in traditional anionic polymerization,<sup>15,16</sup> a reasonable conjecture is that peak 3 corresponds to the contact ion pairs which are the least active and peak 2 corresponds to the loose ion pairs which may be the complex of  $R^-K^+-PEG$ , having moderate activity. The num-

ber of the species corresponding to peak 1 is few, but they are the most active species which can initiate a much faster polymerization process—possibly they are the free carbanions. Since the existence of several active species in the presence of a complexing agent (such as amines and ethers) is the typical characteristic of traditional anionic polymerization, we think that this is the most direct evidence of the anionic polymerization mechanism of the Gilch route. The much wider molecular weight distribution is coincident with the existence of more than one polymerization-active species. Obviously, a higher PEG content will cause more  $R^-K^+$  pairs to be dissociated, and a higher average polymerization degree is anticipated. This trend is clearly seen from the data in Table I.

#### Possible Gelation-avoiding Mechanism

Because of the existence of dissociated carbanions in the system, it is reasonable to quest whether these free carbanions will accelerate the possible interchain nucleophilic substitution by-reactions between carbanions and the  $-\text{CH}(\text{Cl})-$  groups when Cl atoms are not timely eliminated (see Scheme 2). Evidence that is advantageous to this assumption is found from our experimental results. If the dissociation of the contact  $R^-K^+$  ion pairs is only accelerating the polymerization process, a higher PEG content is simply increasing the polymerization degree and has nothing to do with the gelation process. However, with the increased PEG content, gelation reappeared again. On the other hand, disregarding this assumption, we cannot account for the reason why gelation disappeared at a lower PEG content. However, recently, there was a report with respect to this problem, in which structural defects from interchain by-reactions were not detected within the limitation of NMR spectrometer.<sup>12</sup> Therefore, it is still uncertain whether gelation is due to crosslinking. But one of the reasonable explanations of our experimental results is in agreement with the assumed point of view. According to our explanation, the enhanced basicity of the free *t*-BuO<sup>-</sup> is fully considered. The free *t*-BuO<sup>-</sup> will accelerate the elimination reactions of **1-3** (the first elimination) and **4** to MEH-PPV (the second elimination, i.e., the conjugation-formation process). It is noticed that there is a competitive relationship between the conjugation-formation process and the supposed interchain substitutional by-reactions. At a low PEG content, most of



the dissociated anions are  $t\text{-BuO}^-$  and the dissociation of  $\text{R}^-\text{K}^+$  pairs are substantially suppressed due to the existence of a large number of cations from  $t\text{-BuOK}$ . The acceleration of the conjugation-formation process is probably predominant in this case, and the overall effect is advantageous to the suppression of gelation. However, when the PEG content is high, the amount of the dissociated carbanions increases; apart from the accelerating anionic polymerization process, part of these dissociated carbanions will participate in the interchain nucleophilic substitution reactions and lead to the emergence of gelation once again.

## CONCLUSIONS

By introducing PEG into the reaction system, the existence of more types of polymerization-active species was found from the multimodal characteristic of the GPC curves, confirming the dissociation of the carbanion-cation pairs as well as an anionic polymerization mechanism in the Gilch route. The enhanced dissociation of the base ( $t\text{-BuO}^-\text{K}^+$ ) ion pairs by PEG may be responsible for the disappearance of gelation. Free  $t\text{-BuO}^-$  anions accelerate the conjugation-formation process and therefore suppress the interchain by-reactions. The PEG-participated Gilch polymerization has the potential to be widely applied in the large-scale preparation of high-quality soluble PPVs.

The authors acknowledge the financial support of this study from the National Natural Science Foundation of People's Republic of China.

## REFERENCES

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed* 1998, 37, 402, and references therein.
2. Hide, F. H.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc Chem Res* 1997, 30, 430, and references therein.
3. Braun, D.; Heeger, A. J. *Appl Phys Lett* 1991, 58, 1982.
4. Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* 1992, 357, 477.
5. Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* 1995, 269, 1086.
6. Cater, S. A.; Scott, J. C.; Brock, P. J. *Appl Phys Lett* 1997, 71, 1145.
7. Wudl, F.; Allemand, P. M.; Srdanov, G.; Ni, Z.; McBranch, D. ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991; p 683.
8. Andersson, M. R.; Yu, G.; Heeger, A. J. *Synth Met* 1997, 85, 1275.
9. Spreitzer, H.; Becker, H.; Kluge, E.; Kreuder, W.; Schenk, H.; Demand, R.; Schoo, H. *Adv Mater* 1998, 10, 1340.
10. Gilch, H. G.; Wheelwright, W. L. *J Polym Sci Part A Polym Chem* 1966, 4, 1337.
11. Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* 1997, 30, 8094.
12. Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* 1999, 32, 4925.
13. Wudl, F.; Srdanov, G. U.S. Patent 5 189 136, 1993.
14. Burn, P. L.; Kraft, A.; Baigent, D. R.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Jackson, R. W. *J Am Chem Soc* 1993, 115, 10117.
15. Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *Polymer* 1964, 5, 54.
16. Beylen, M. V.; Bhattacharyya, D. N.; Szwarc, M. *J Phys Chem* 1966, 70, 157.