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A new approach for the synthesis of conjugated/non-conjugated poly(phenylene vinylene)–polyacrylamide copolymers

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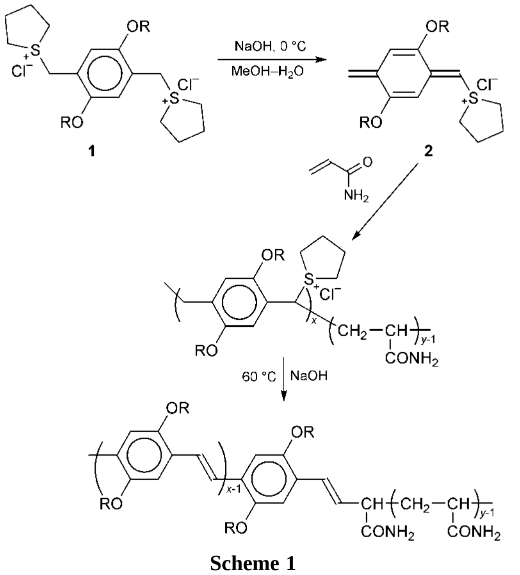
A new type of poly(phenylene vinylene)–polyacrylamide copolymer has been synthesized by a modified sulfonium precursor route; the obtained copolymer is composed of hydrophobic PPV conjugated blocks and hydrophilic polyacrylamide segments; these two parts show strong phase separation and produce a multiphase structure in the solid state.

Some of the most promising candidates for the active layer in organic light-emitting diodes (LEDs) are polymers derived from poly(phenylene vinylene) (PPV).[1–5] Fully conjugated PPV derivatives often show low luminescent efficiencies owing to non-radiative decay resulting from the movement of excitons to quenching centers.[6,7] Exciton confinement can be achieved by preparing a polymer with low HOMO–LUMO gap energy blocks in between high ones. Therefore, attention has been paid to synthesizing conjugated/non-conjugated PPV derivatives. One way to realize this structure is to interrupt the conjugation of the polymer at short intervals with non-conjugated segments by sample modification during PPV synthesis.[8,9] Another way to obtain a polymer with well defined fluorescent units makes use of a Wittig condensation of an arylene bisphosphonium salt with a spacer containing bis(benzaldehyde).[10–12]

Recently, we found a new method for the synthesis of such copolymers. Our method originated from investigating the mechanism in the sulfonium precursor route (SPR) to PPV derivatives established by Wessling and Zimmerman.[13,14] We observed what happened when water-soluble monomer acrylamide (Am) was added in the polymerization of bis(sulfonium) compound **1** in an aqueous system, and found that copolymerization occurred in which the *p*-quinodimethane intermediate **2** might act as both monomer and free radical initiator. Scheme 1 outlines the process of the formation of PPV/polyacrylamide copolymers. Obviously, this copolymerization strongly supports a free radical mechanism for SPR. In fact, the copolymerization proceeds so well that the color of the product can be tuned by the feed ratio of two monomers. In other words, the conjugated length of the PPV blocks is shortened by the incorporation of polyacrylamide (PAm) segments in between. Furthermore, this kind of copolymerization also offers an opportunity to prepare amphiphilic polymers which may be very useful for self-assembly into ultrathin films and nanocomposites.



Scheme 1

The copolymers were synthesized through the following procedure: under vigorous stirring and nitrogen atmosphere, a solution of bis(sulfonium) salt **1** (1.04 g, 2 mmol) in MeOH (10 ml) was added dropwise to a solution of acrylamide and NaOH (0.08 g, 2 mmol) in 25 ml of water. The temperature was kept at 0 °C for 1 h. Then additional aqueous NaOH (0.5 M, 10 ml) was added, and the reaction mixture was heated to 60 °C for another hour. An orange precipitate was obtained and filtered off. After washing well with water and MeOH, the product was dried *in vacuo*. When the amount of acrylamide exceeded 20 g the produced copolymer was water-soluble. The polymer was purified by dialyzing against water for three days (3 × 1000 ml) to remove unreacted monomers and some acrylamide homopolymer (polymers with molecular weight of less than 12 000 were removed). The final solution was poured into a large amount of MeOH, and a pale yellow polymer was obtained and washed with refluxing MeOH and then dried *in vacuo*. Except for the water-soluble copolymer, the other polymers show poor solubility in solvents such as THF and DMF, probably owing to hydrogen bonding between amide groups. However, they are partially soluble in $CHCl_3$, which allows the photoluminescence (PL) spectra to be obtained. Such a low solubility, however, is not sufficient for GPC measurements. Therefore we focused our attention on the viscosity of the water-soluble copolymer at various concentrations and the GPC result obtained in aqueous solution. The composition of the copolymers were calculated according to the amount of nitrogen obtained by elemental analysis.

Table 1 summarizes the results of copolymerizations for different concentrations of acrylamide. With an increase in the amount of acrylamide in the reaction system, the weight percentage of PAm segments in the copolymers increase, while the product changes from red to pale yellow, and the PL peak shifts from 550 nm (yellow) to 509 nm (green). All these data showed that the conjugation length of the PPV block became shorter as more Am units were inserted into the polymer chain. However, even when a large excess of acrylamide was added to the reaction system, we failed to produce a copolymer with sufficiently short conjugated lengths of PPV blocks to produce blue luminescence. It seems that the present copolymerization is quite different from those in traditional free radical copolymerizations for vinyl monomers. The *p*-quinodimethane intermediate **2** shows a strong tendency to undergo homopolymerization even under very dilute concentrations and in the presence of a large excess of Am. The FTIR spectra of all the prepared copolymers support the structure of copolymer suggested. Peaks characteristic of PPV blocks such as at 1203 cm^{-1} (C–O stretching), 2961 cm^{-1} (C–H stretching of CH_3) and 970 cm^{-1} (C–H bending of *trans* vinylene) can be clearly

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Table 1 Results of copolymerizations using various amounts of acrylamide

Sample	Acrylamide/g	Weight of polymer obtained/g	Colour	PAm segemnt (wt%)	Solubility (in $CHCl_3$)	λ_{max} (PL) ($CHCl_3$)/nm
1	0	0.76	Red	0	Soluble	550 (λ_{ex} = 420 nm)
2	5	1.05	Red–orange	38	Slightly soluble	542 (λ_{ex} = 420 nm)
3	10	1.58	Orange	47	Slightly soluble	536 (λ_{ex} = 420 nm)
4	15	2.46	Yellow	64	Slightly soluble	524 (λ_{ex} = 420 nm)
5	20	3.85	Pale yellow	82	Water-soluble	509 (H_2O) (λ_{ex} = 400 nm)

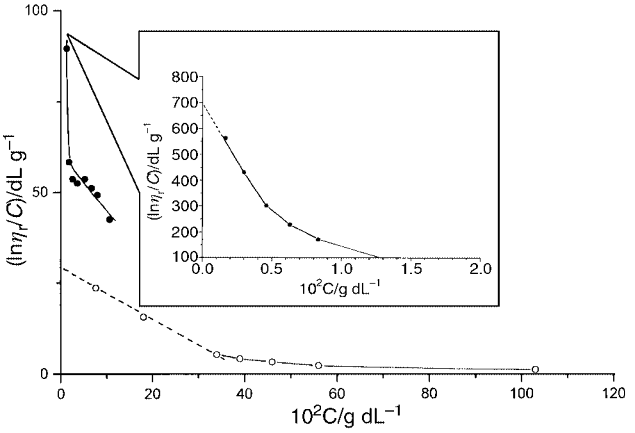

Fig. 1 The dependence of lnη_r/C on the concentration of polyacrylamide (○) or copolymer (●) in water at 30 °C.

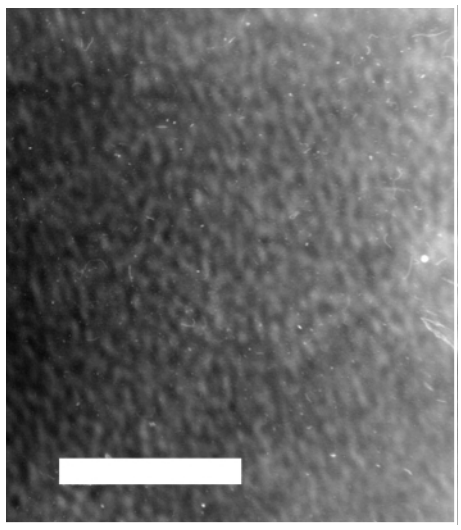

Fig. 2 TEM image of poly[2,5-bis(heptyloxy)phenylene vinylene-*co*-Ba(acrylate)$_2$]. The white bar corresponds to 20 nm.

observed. Signals from PAm segments including at 3400 cm^{-1} (wide band, N–H stretching of amide) and 1669 cm^{-1} (C=O stretching of amide) also appear in the spectra.

Fig. 1 shows the viscosity of the water-soluble copolymer and pure PAm measured at different concentrations in water at 30 °C; η_r is the relative viscosity using water as a reference. The insert is an enlarged plot for the copolymer at very low concentration. For both polymers, the value of lnη_r/C increases sharply as the concentration of polymer approaches zero. Obviously, the viscosity of the copolymer is higher than that of PAm at any concentration. By extrapolation of lnη_r/C to C = 0, it is seen that the intrinsic viscosity of the copolymer ([η] = 700 dL g^{-1}) is 24 times as high as that of PAm ([η] = 28 dL g^{-1}). According to the formula $[\eta] = KM_\eta^\alpha$ ($K = 6.31 \times 10^{-3}$, α = 0.80, T = 30 °C),[15] M_η of PAm is calculated as 3.46×10^4. Owing to the absence of a relationship between M_η and [η], an exact value of M_η of the copolymer could not be obtained. We also studied M_w of the two polymers by GPC using sulfonated polystyrene as a standard in aqueous medium. The result showed that M_w of PAm and the copolymer were 4.12×10^4 and 9.67×10^4, respectively, with a PDI of 2.13 and 2.74, respectively. If we calculate the M_η of the copolymer using the relation KM_η^α, the result is 2×10^6, much higher than M_w of the copolymer measured by GPC. The above result confirmed that a high molecular weight copolymer was produced by copolymerization. The extraordinarily high viscosity of the copolymer may well be due to the presence of rod-like and alkyl chain-bearing PPV blocks which can aggregate with each other and form hydrophobic domains in aqueous medium. These domains are dispersed in solution and act as solid particles, or on the other hand, as physically cross-linking joints which link PAm segments to form a network and therefore considerably lower the mobility of the polymer solution. A multiphase structure in the solid state was revealed by TEM observation after hydrolysis of the copolymer in KOH solution and then treating with $BaCl_2$. Barium ions were introduced to increase the contrast of the two microphases in electron transmission. Fig. 2 is a TEM photograph of the Ba^{2+}-modified copolymer which can be denoted as poly[2,5-bis(heptyloxy)phenylene vinylene-*co*-Ba(acrylate)$_2$]. The light regions correspond to the hydrophobic domains occupied by PPV blocks, while the dark regions correspond to the hydrophilic phase mainly composed of poly[Ba(acrylate)$_2$] segments. The size of these domains is in the range of several nanometers. Since the conjugated and non-conjugated blocks are randomly arranged in the copolymer the formed multiphase structure is disordered. The above two results indicate that the copolymer has a rod/coil structure in which the two different units are not statistically distributed along the main chain.

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