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Copolymerization of *N*-Vinylcarbazole and Vinyl Acetate via Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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Summary: The reversible addition–fragmentation chain transfer (RAFT) random copolymerization of *N*-vinylcarbazole (NVC) and vinyl acetate (VAc) was carried out using *s*-benzyl-*o*-ethyl dithiocarbonate (BED) as the chain transfer agent and 2,2′-azoisobutyronitrile (AIBN) as the initiator in 1,4-dioxane solution at 70 °C. The polymerization showed the characteristics of 'living' free radical polymerization behaviors: first order kinetics, linear relationships between molecular weight and conversion, and narrow polydispersity of the polymers. The reactivity ratios of NVC and VAc were calculated via the Kelen–Tudos (KT) and non-linear error in variable (EVM) methods and showed as $r_1 = 1.938 \pm 0.191$, $r_2 = 0.116 \pm 0.106$. The thermal behavior of the copolymers with different content of NVC and VAc was investigated by DSC and TGA. The results showed that the introduction of a VAc segment into copolymer significantly reduced the T_g of the NVC homopolymers. FT-IR spectra, fluorescence spectra, and cyclic voltammetric behavior of these copolymers were also measured and compared with those of NVC homopolymers. The copolymers showed similar oxidative behavior to the NVC homopolymer. However, there was only one reductive potential peak shown for the copolymers at about 0.058 V.

Keywords: copolymerization; N-vinylcarbazole; reversible addition-fragmentation chain transfer (RAFT); vinyl acetate

Introduction

Poly(*N*-vinylcarbazole) (PVK) is a well known photoconductor polymer.[1] Since the first success of PVK in electrophotographic applications, numerous studies have been devoted to carbazole-containing polymers.[2] Recent developments in this field are mostly connected to the applications in polymeric light-emitting diodes,[3] organic photorefractive materials,[4] and photovoltaic devices.[5] The widely used PVK can be easily manufactured via cationic polymerization or radical polymerization.

Controlled/'living' radical polymerizations (LRPs) demonstrate both the benefits of conventional free radical polymerization and the capability to prepare well-defined macromolecular architectures of living polymerization techniques.[6–8] This technique allows the preparation of functional polymers with pre-determined molecular weight and topologic structures, such as block, graft, and star polymers, in a facile way. The well-developed LRP methods include atom transfer radical polymerization (ATRP),[6] nitroxide-mediated radical polymerization (NMP),[7] and reversible addition–fragmentation chain transfer (RAFT)[8] polymerization. Several reports describe attempts to synthesize PVK in a controlled way via LRP techniques. For example, Fukuda et al. explored the polymerization of *N*-vinylcarbazole (NVC) under typical NMP conditions.[9] A negative

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result for the homopolymerization of NVC was shown, while a positive result was observed for the copolymerization of NVC and styrene. Similar results were also reported by Schmidt-Naake et al.[10] By using acetic anhydride as an accelerator, Nowakowska et al. demonstrated the successful preparation of poly(sodium styrenesulfonate-*block*-NVC) in a controlled way via NMP techniques.[11] The ATRP technique also has been used for the synthesis PVK in a controlled way. By selecting $C_{60}Cl_n$/CuCl/Bpy as the initiating system, Chen et al. successfully prepared a C_{60}-centered PVK star polymer with a narrow molecular weight distribution ($M_w/M_n = 1.33$).[12] The same group also reported the preparation of block copolymer, poly(NVC- *block*-styrene), via an ATRP technique.[13] The obtained PVK shows bimodal molecular weight distributions. By optimizing the initiating system, Brar et al. successfully carried out the atom transfer radical homopolymerization of NVC using Cu^I/Cu^{II}/Bby as a catalyst system.[14] The results showed the typical characteristics of a controlled radical polymerization. Detailed polymerization kinetics were investigated. With regards to the RAFT polymerization of NVC, Endo and co-workers were the first to report the controlled synthesis of PVK with predetermined molecular weights and a narrow polydispersity by the xanthate-mediated controlled radical polymerization.[15]

Here, we report the copolymerization of NVC with vinyl acetate (Vac) by RAFT polymerization. The introduction of poly(vinyl acetate) (PVAc) into the PVK chain can greatly reduce the T_g of PVK and improve it's mechanical properties at low temperature. The RAFT polymerization technique ensured control of the resultant polymer structure. The fluorescence spectrum, UV-vis spectrum, and cyclic voltammetry of the obtained polymer were investigated. Relationships between these properties and the copolymer's composite content were also explored. The results showed that the obtained polymers had a lower T_g than PVK while possessing similar photoresponsibilities to PVK.

Experimental Part

Materials

N-Vinylcarbazole (NVC, Acros, USA, 98%) was recrystallized from methanol. 2,2′-Azoisobutyronitrile (AIBN) (Shanghai Chemical Reagent Co. Ltd, China, 99%) was purified by recrystallization from ethanol and dried under vacuum at room temperature overnight. 1,4-Dioxane (Shanghai Chemical Reagent Co. Ltd., China, 99%) was distilled from sodium wire, and toluene (Shanghai Chemical Reagent Co. Ltd., China, 99%) was distilled before use. Vinyl acetate (VAc) (Shanghai Chemical Reagent Co. Ltd., China, 99%) was purified by drying with $CaC1_2$ and was fractionally distilled under nitrogen, and then refluxed briefly with a small amount of benzoyl peroxide and redistilled under nitrogen. The RAFT agent, *s*-benzyl-*o*-ethyl dithiocarbonate (BED), was synthesized by the reaction of potassium *o*-ethyl dithiocarbonate with benzyl bromide in ethanol according to the procedure reported in the literature.[16] All other materials were used without further purification.

Polymerizations

The following procedure was typical. VAc (0.5 mL, 5.54 mmol), a master batch of VAc (5 mL, 55.4 mmol), BED (234.9 mg, 1.108 mmol), and AIBN (36.3 mg, 0.222 mmol) were dissolved in 10 mL of 1,4-dioxane. Aliquots of 1.5 mL were then added into a 5 mL ampoule which was pre-loaded with 1.07 g (5.54 mmol) of NVC. The content was purged with argon for approximately 10 min to eliminate the oxygen. The ampoules were then flame sealed. The polymerization reaction was performed at the appropriate temperature. After the determined reaction time, each ampoule was quenched in ice water, and opened. The reaction mixture was diluted with 1,4-dioxane (about 2 mL), and precipitated into a large amount of *n*-hexane (about

200 mL). The polymer was obtained by filtration and dried at room temperature under vacuum to a constant weight. Conversion of styrene was determined gravimetrically.

Characterization

The molecular weights (M_ns) and polydispersity indexes (PDIs) of the polymers were determined with a Waters 1515 gel permeation chromatograph equipped with a refractive index detector, using HR 1, HR 3, and HR 4 columns with a molecular weight range of 100–500 000 calibrated with polystyrene standard samples and operated at 30 °C. Tetrahydrofuran (THF) was used as the eluent at a flow rate of $1.0\,\mathrm{mL \cdot min^{-1}}$. ^{1}H NMR spectra of the polymers were recorded on an INOVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. FT-IR spectra were measured using a Varian Scimiter 1000 with the sample dispersed in KBr pellets. Ultraviolet–visible (UV-vis) and fluorescence spectra were measured with a Varian Cary 50 and a Varian Cary Eclipse. The thermal stability was determined with a TA 2010 thermogravimetric analyzer at a heating rate of $20\,^\circ\mathrm{C \cdot min^{-1}}$ in nitrogen. Cyclic voltammetry (CV) of the polymer film on a Pt disk electrode was scanned anodically and cathodically in a 0.1 M acetonitrile solution of tetrabutylammoniumhexafluorophosphate (n-Bu_4NPF_6) with Ag/Ag^+ and a platinum wire as the reference and counter electrodes, respectively. A 631B analyzer (manufactured by Shanghai Zhenghua analysis instrument Co. Ltd., China) was used for the measurements.

Results and Discussions

The key point for a successful RAFT polymerization is the selection of RAFT agent with suitable structure. Mori et al. reported that the successful RAFT polymerization of *N*-vinyl cabazole (NVC) can be performed using a xanthate type compound as the chain transfer agent (CTA). At the same time, vinyl acetate (VAc) can also be polymerized in a controlled manner using a xanthate as CTA. Here, a xanthate, *s*-benzyl-*o*-ethyl dithiocarbonate (BED), was selected as the CTA to carry out the RAFT copolymerization of NVC and VAc using AIBN as the initiator in 1,4-dioxane solution. The polymerization kinetics are shown in Figure 1. The monomer conversions of the polymerization increased with polymerization time. An S-shape relationship between $\ln([M]/[M]_0)$ and reaction time was obtained. The monomers

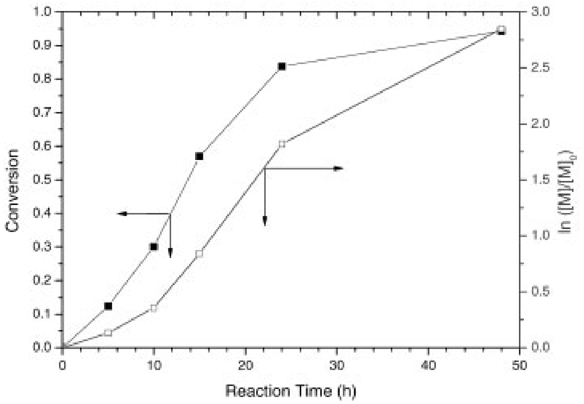

Figure 1.
Plots of $\ln([M_0]/[M])$ and conversion versus reaction time in the RAFT copolymerization of NVC and VAc using BED as the RAFT agent and AIBN as the initiator at 70 °C. Reactant feed molar ratio: [NVC]/[VAc]/[BED]/[AIBN] = 250:250:5:1.

were almost full converted into polymer (94%) after 48 hours reaction under 70 °C.

The dependence of the number average molecular weights (M_n) and polydispersity indexes (PDI) on monomer conversion are shown in Figure 2. It shows that the M_ns increased linearly with monomer conversion. The M_ns from GPC results were slightly higher than the corresponding theoretical values ($M_{n(th)}$) ($M_{n,th} = [\text{monomer}]_0/[\text{BED}]_0 \times \text{conversion} \times M_{\text{monomer}}/2 + M_{\text{BED}}$, BED, where $[\text{monomer}]_0$ and $[\text{BED}]_0$ are the initial concentrations of the monomer and RAFT agent, respectively, and M_{monomer} and M_{BED} are the molecular weights of the monomer and RAFT agent, respectively.), which could be due to incomplete usage of RAFT agent. On the other hand, the GPC standard calibration samples of polystyrene may be another cause of the deviation from the theoretical values of M_n obtained by GPC. In all cases, the PDIs of the polymers were lower than 1.4, which corresponds to different conversions.

All the above results show that the copolymerization of NVC and VAc mediated by BED represent 'living'/controlled free radical polymerization characteristics. Polymers with pre-determined molecular weight and narrow polydispersity were obtained successfully. In order to calculate the reactivity ratios of NVC and VAc under the RAFT polymerization, the copolymerization of these two monomers was further investigated under different feeding monomer ratios. The result is shown in Table 1.

Reactivity ratios for the comonomers were calculated using the Kelen–Tudos (KT)[17] and non-linear error in variable (EVM) methods. In this case, the reactivity ratios were $r_1 = 1.938 \pm 0.191$ and $r_2 = 0.116 \pm 0.106$ at 70 °C. As was shown by Ushakov and Nikolaev, vinyl acetate and vinylcarbazole from a copolymer with conventional free radical copolymerization initiated by AIBN at 65 °C resulted in reactivity ratios of $r_1 = 2.680$ and $r_2 = 0.338$.[18,19] The difference between these two couple values may be caused by different polymerization conditions, e.g., solvent and temperature.

The UV-vis spectra of the polymers with different PVK content were determined (Figure 3) in toluene solution. The molar concentration of these polymer solutions were the same, which evidently resulted in a lower absorption of carbazole characteristic peaks in the low carbazole content polymers. Thus, the UV-vis absorption strength was decreased from PVK to PVKVAc4.

The Fourier transform infra-red (FT-IR) spectra of vinylacetate and the vinylcarbazole copolymer (PVKVAc1) was measured

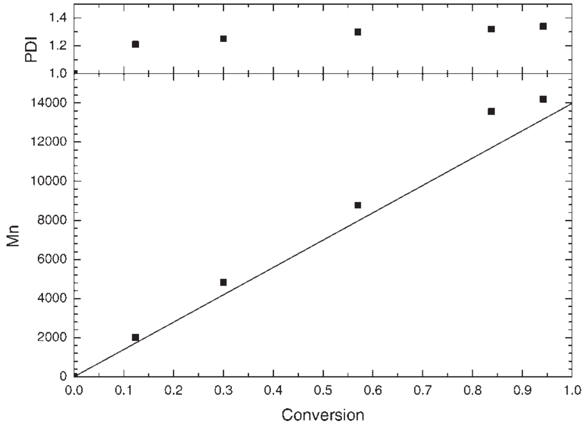

Figure 2.

Plots of number-average molecular weight (M_n) and polydispersity index (PDI) versus conversion in the RAFT copolymerization of NVC and VAc using BED as the RAFT agent and AIBN as the initiator at 70 °C. Reactant feed molar ratio: [NVC]/[VAc]/[BED]/[AIBN] = 250:250:5:1.

Table 1.
Results summary of RAFT copolymerization of vinyl carbazole with vinyl acetate [a]

Label	monomer ratio (molar ratio)		Conv.(%)	polymer composition[b] (molar ratio)		Mn[c]	PDI[c]	Tg[d] (°C)
	M_1(VK)	M_2(VAc)		PVK	PVAc			
PVK	1	0	91	1	0	18 200	1.22	179.4
PVKVAc1	3	1	84	2.8	1	15 800	1.31	178.6
PVKVAc2	2	1	90	1.6	1	14 500	1.33	171.1
PVKVAc3	1	1	86	0.8	1	11 800	1.3	162.3
PVKVAc4	0.5	1	82	0.4	1	9100	1.35	160.6

[#] Polymerization were carried out with [monomer]:[RAFT]:[AIBN] = 1000:8:1 at 70 °C for 24 hours, RAFT agent: S-benzyl O-ethyl carbonodithioate;

[b] Measured by elementery analysis;

[c] Measured by GPC with polystyrene as the reference;

[d] Onset point.

and compared with that of the vinylcarbaole homopolymer (PVK) (Figure 4). The copolymer showed characteristic peaks of PVK. Furthermore, an additional peak at 1730 cm^{-1} was observed in the spectrum of PVAVAc1, which can be attributed to the existence of the carbonyl group in the vinylacetate segments.

PVK is a material with good heat resistance properties. The insertion of vinylacetate segments into the PVK chain may result in a decrease of heat resistance. Thus, the thermal stability of these polymers was characterized and is shown in Figure 5. The results of TGA suggest that all the polymers have good thermal stability. The onset decomposition temperatures (T_d) ranged from 356 to 386 °C under a nitrogen atmosphere. The polymers show sharp weight loss at a temperature higher than 400 °C, which indicates the decomposition of the polymer backbones. Increasing the VAc content in the copolymer resulted in a minor decrease of the heat stability.

The carbazole-containing material showed strong fluorescence. The fluorescence spectra of PVK and PVAVAc2 were

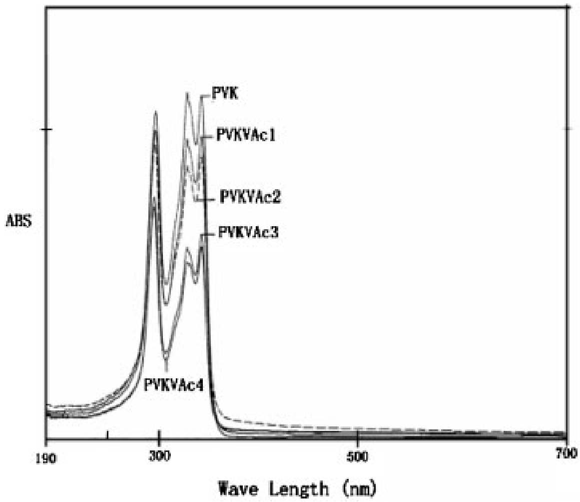

Figure 3.
UV-vis spectra of vinylacetate and vinylcarbazole copolymer in toluene solution at room temperature. The concentration of polymers were set to 5×10^{-6} mol/L.

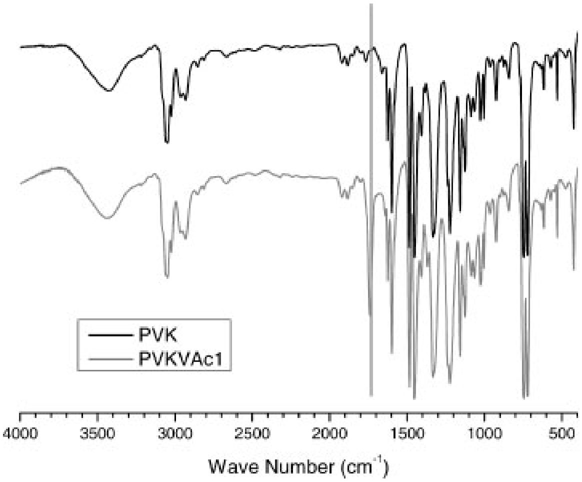

Figure 4.
Fourier transform infra-red (FT-IR) spectra of the PVK and PVKVAc1 polymers.

determined as showed in Figure 6. Both PVK and PVKVAc2 showed characteristic fluorescence emission with a peak of 373 nm when excited by a 300 nm light in toluene solution. A stronger fluorescence peak observed for the PVK solution compared to that of the PVKVAc2 solution was a result of the more greater amount of carbazole groups in PVK than in PVKVAc2. The introduction of VAc segments into the PVK chain did not change the fluorescence properties of PVK.

The influence of VAc segments on the copolymer's electroproperties was characterized by cyclic voltammetry. The results are shown in Figure 7. All the copolymers show slightly higher oxidative onset potentials than that of the PVK homopolymer. The introduction of VAc to the PVK polymer chain resulted in a big difference in reductive behavior. The PVK homopolymer showed two comparable reductive potential peaks at about 0.913 and 0.058 V, respectively. In the cases of the vinylacetate

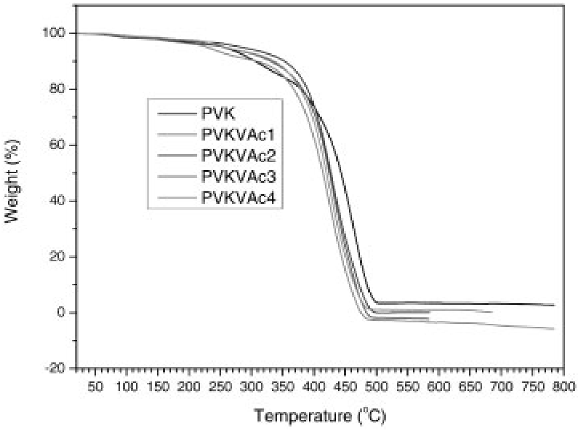

Figure 5.
Thermal gravimetric analysis (TGA) curves of the polymers. Under nitrogen atmosphere with 100 mL min^{-1} at a heating rate of 20 °C min^{-1}.

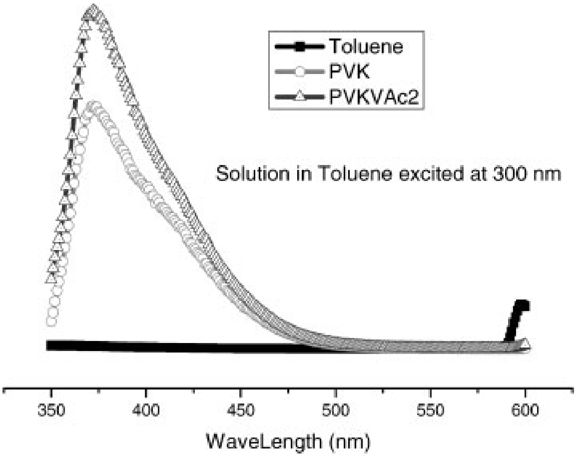

Figure 6.
Fluorescence spectra of polymers in toluene at room temperature with molar concentration of 1×10^{-6} mol · L^{-1} and excited at 300 nm.

and vinylcarbazole copolymer, there was only one reductive potential peak at about 0.058 V, which was same as one of the PVK homopolymer reductive peaks. Increasing the vinylacetate content in the copolymers caused an increase of the reductive peak area.

Conclusions

By choice of BED as the chain transfer agent and AIBN as the initiator, the RAFT random copolymerization of NVC and VAc was successfully carried out in 1,4-dioxane solution at 70 °C. The reactivity ratios of NVC and VAc were calculated via the Kelen–Tudos (KT) and non-linear error in variable (EVM) methods and were calculated as $r_1 = 1.938 \pm 0.191$, $r_2 = 0.116 \pm 0.106$. The copolymers show a similar or very minor decrease in heat resistance and fluorescence properties compared with the NVC homopolymer. The introduction of VAc segments into the copolymer significantly reduced the T_g of PVK, which would

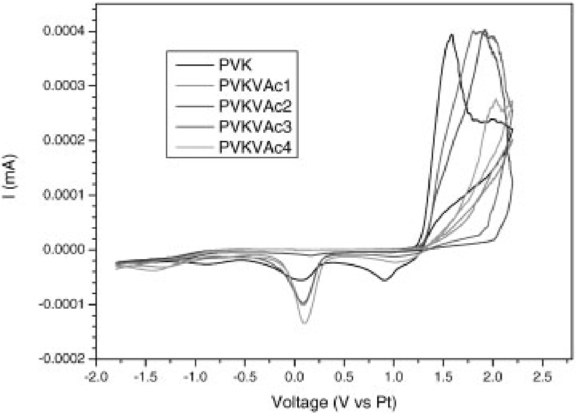

Figure 7.
Cyclic voltammograms of the polymers recorded from thin films coated on platinum plate electrodes in an electrolyte solution of n-Bu_4NClO_4 (0.1 M) in acetonitrile, with Ag/AgCl (0.1 M) as the reference electrode, at room temperature. Scan rate = 50 mV s^{-1}.

improve the mechanic property at low temperature of such PVK-containing materials. However, the copolymer showed different reductive potentials compared to the PVK homopolymer. A further investigation of the use of such copolymers as photoelectric material will be done in the following work.

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