Polymer Bulletin 55, 181–189 (2005)
DOI 10.1007/s00289-005-0429-7

Polymer Bulletin

Novel Hyperbranched predominantly Alternating Copolymers Made From A Charge Transfer Complex monomer pair of p-(chloromethyl)styrene and Acrylonitrile via Controlled Living Radical Copolymerization

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Received: 14 April 2005 / Revised version: 27 June 2005 / Accepted: 21 July 2005

Summary

Novel hyperbranched copolymers were successfully synthesized by the controlled charge transfer complex inimer and living radical copolymerization of p-(chloromethyl)styrene (PCMS) and acrylonitrile (AN). The resulting copolymers were characterized by SEC, NMR, FTIR, DSC and elemental analysis etc.. The influences of reaction conditions, such as the polymerization temperature, the catalyst (CuBr) concentration and the monomer ratio, on the resulting copolymers were investigated in detail. The monomer reactivity ratios were evaluated to be $r_{PCMS} = 0.937$ and $r_{AN} = 0.088$ respectively by the Fineman-Ross method. The higher are the polymerization temperature and the ratio of catalyst to monomer, the higher is the branching degree of the resulting copolymer. When the amount of monomer AN was used in excess than that of the monomer PCMS in the raw feed, the hyperbranched predominantly alternating copolymers HP[PCMS-co-AN] could be obtained. These hyperbranched copolymers were successfully used as functional macroinitiators to synthesize the star-shaped poly(PCMS-co-AN)/poly(MMA) block copolymers.

Introduction

In recent years, hyperbranched polymers have attracted considerable attention due to their properties similar to dendrimers, such as highly branched, highly functionalized, low viscosity, and three-dimension globular structure. Hyperbranched polymers can be prepared conveniently by a one-step polymerization process in large scale with relatively low cost[1~6]. Traditionally, the majority of hyperbranched polymers had been prepared by polycondensation of AB_2 type monomers. In 1995, Fréchet et al. reported a new synthetic route to prepare hyperbranched polymers, which was termed self-condensing vinyl polymerization (SCVP) [7]. The monomers used in SCVP are having bifunctional structure AB*, where A stands for a double bond and B* represents an initiating site, and are termed 'inimer'. Afterward, this approach has been expanded to various types of living polymerizations, e.g. ATRP[8~10], nitroxide-mediated radical polymerization[11], ring-opening polymerization[12], and group transfer polymerization[13]. But there is a severe limitation of this approach because only a few suitable inimers are available.

On the other hand, copolymerization is a convenient and common method for modifying and improving the polymer properties to meet some requirements of new applications. The copolymerization of a charge transfer complex (CTC), which is formed by an electron rich monomer and an electron deficient monomer, is an ideal situation to synthesize copolymers with predominantly alternating structure [14]. These copolymers can exhibit some interesting physical and mechanical properties ascribing to their alternating structure [15]. Matyjaszewski and coworkers reported the controlled copolymerization of electron rich monomers (e.g. isobutene) with electron deficient monomers (e.g. butyl acrylate) by ATRP[16]. Recently, They further researched the living copolymerization of styrene and AN by ATRP[17]. Li et al. subsequently studied the copolymerization of styrene with N-substituted maleimides by ATRP and the copolymerization was found in a controlled or "living" process and the structure of the copolymer was predominantly alternating [18].

In previous papers, we have successfully prepared some hyperbranched alternating copolymers using p-(chloromethyl)styrene as an inimer to form CTC with a common vinyl monomer, such as chlorotrifluoroethylene and N-cyclohexylmaleimide, by controlled radical polymerization[19,20]. In this paper, we further investigate p-(chloromethyl)styrene as an inimer to form CTC with another common vinyl monomer acrylonitrile (AN) to synthesize some novel hyperbranched predominantly alternated copolymers by controlled ATRP. And then using one of these novel hyperbranched copolymers as a core to synthesize star-shaped poly(PCMS-co-AN)/poly(MMA) block copolymer is also discussed.

Experimental

Materials

PCMS and AN were obtained from Acros and the inhibitor was removed by passage through a column of neutral alumina. CuBr (A.R. grade) was washed repeatedly with acetic acid and ethanol, and then dried under vacuum. 2, 2'-bipyridine and benzene (A.R. grade) were received from Shanghai Reagent Co. and used without purification.

Instruments

The composition of the resulting copolymers was calculated from nitrogen elemental analysis (Elementar Vario EL). ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Mercuryplus 400 NMR spectrometer at room temperature with $CDCl_3$ as solvent. The glass transition temperatures (T_g) were measured by differential scanning calorimetric (DSC) (Perkin Elmer Pyris-1 Series) in a flowing nitrogen atmosphere (the heating rate was 20°C/min). The molecular weights of the resulting copolymers were determined by size exclusion chromatography (SEC) (Waters 150, USA) equipped with single RI detector (Waters 410) and were calibrated universally by linear polystyrene standards. The eluent was THF with a flow rate of 1ml/min. The absolute molecular weights of the resulting copolymers were determined in THF on a Waters 150 SEC apparatus, equipped with an Optilab DSP differential refractometer and a miniDAWN multi-angle (18-angles) laser light scatter detector (Wyatt Technology Co.), and operating at $\lambda = 690$ nm. The FTIR spectra were recorded on a

Perkin Elmer Paragon 1000 FTIR spectrometer using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr. UV/Vis spectra were recorded on a Perkin Elmer Lambda 20/2.0 UV/Vis spectrometer.

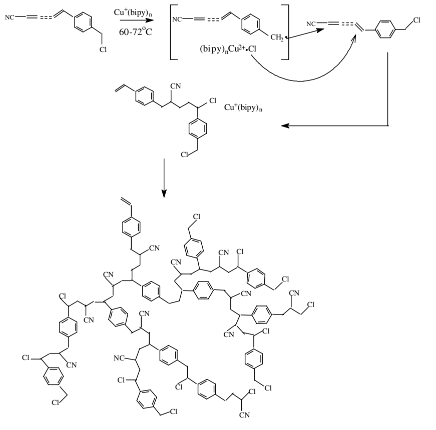
Polymerization

A typical polymerization was shown as below: CuBr (0.0500g, 0.349mmol) and 2, 2'-bipyridine (0.1633g, 1.046mmol) were added into a dry flask with a magnetic flea. The flask was sealed with rubber septum and deal with vacuum-nitrogen cycle three times to remove the oxygen. Then benzene (2.4mL) and AN (0.6mL, 9.0mmol) were added to the reactor under nitrogen. Finally, PCMS (1.4mL, 8.9mmol) was charged into the flask through a measuring cylinder. Unless otherwise stated, the molar ratio (PCMS/AN) was 1. The reaction mixture was stirred and heated at 60°C. After polymerization for a given time, the flask was cooled to the room temperature and the rubber septum was removed to allow the catalyst losing activity by oxidization. The mixture in the flask was poured into a large amount of methanol under rapidly stirring to precipitate. The precipitated copolymer was filtered and washed with methanol. Then the precipitated copolymer was dissolved in 50mL $CHCl_3$ and filtered through silica gel to remove the insoluble salts. The filtrate was concentrated and poured into excess methanol again. The precipitated copolymer was collected by filtration and dried under vacuum at 50°C for at least 24h. The monomer conversion was determined by the gravimetric approach.

Results and Discussion

Hyperbranched copolymers of PCMS and AN

AN is a typical electron deficient monomer, which can be polymerized by a free radical mechanism and has been incorporated in alternating copolymers with tri-n-butylstannyl acrylate[21]. PCMS is an inimer that has been used in the synthesis of hyperbranched polymers by the cationic polymerization and ATRP[8,9]. Simultaneously, PCMS is a typical electron rich monomer, which is capable of forming a CTC monomer pair with the electron deficient monomers, such as AN. We have used the benzylic chloride of PCMS as an initiator for ATRP of the CTC (Scheme 1). The general polymerization mechanism is expected to be the controlled SCVP.



Scheme 1

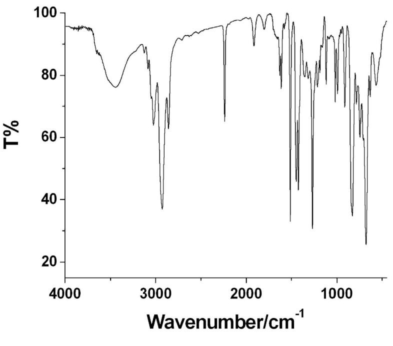


Figure 1 FTIR spectrum of HP(PCMS-co-AN)8

From the FTIR spectrum of the hyperbranched copolymer (Figure 1), the peaks at 3026, 1612, 1512, 1446, 1268, 912, 828cm^{-1} attributed to the benzene ring, the peaks at 2927.8, 2860cm^{-1} attributed to -CH$_2$, the peak at 678cm^{-1} attributed to C-Cl and the peak at 2237.7cm^{-1} attributed to nitrile group of AN were observed, which confirmed the successful copolymerization of PCMS and AN.

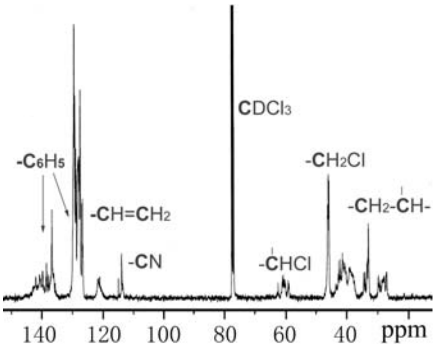


Figure 2 ^{13}C-NMR spectrum of HP(PCMS-co-AN)$_8$

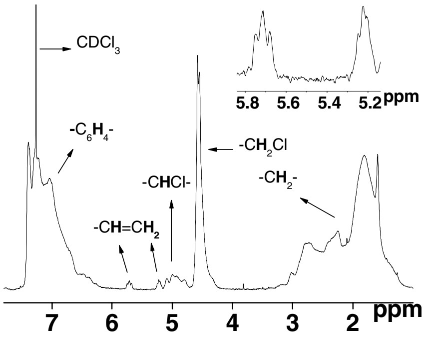


Figure 3 ^{1}H-NMR spectrum of HP(PCMS-co-AN)$_8$

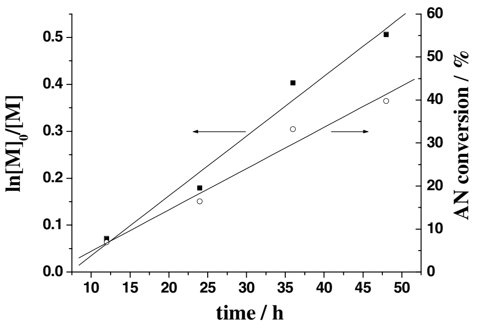


Figure 4 Time dependence of ln[M]$_0$/[M] and AN conversion in benzene at 60°C[PCMS]$_0$=[AN]$_0$=2M, [bipy]$_0$=3[CuBr]$_0$=0.24M; [M]$_0$=[AN]$_0$, [M]=[AN]

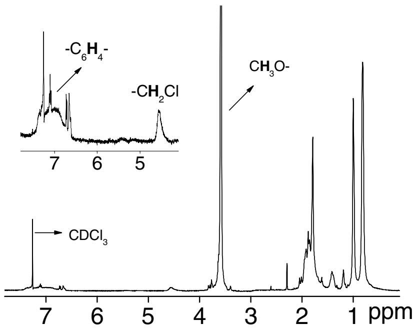


Figure 5 ^{1}H NMR spectrum of star-shaped poly(PCMS-co-AN)$_5$/poly(MMA)

The ^{13}C-NMR spectra of the hyperbranched copolymers further confirmed the successful copolymerization of PCMS and AN. For example HP(PCMS-co-AN)$_8$ (Figure 2), all the resonance signals corresponding to the structure of the hyperbranched copolymer were observed, such as 144-136ppm and 129-127ppm (benzene ring), 121ppm (methylene of the double bond at the chain end), 114ppm (-CN), 62-59ppm(-CHCl-), 46ppm (-CH$_2$Cl), 43-27ppm (methylene and methine of the copolymer chains). At the same time, its ^{1}H-NMR spectrum was shown in Figure 3. The first set of signals, at 5.2 and 5.6ppm, can be attributed to the two methylene protons of the terminal double bond. The second set of signals at 4.4-5.1ppm is typical of the methylene protons adjacent to chlorine atoms. Very broad peaks are observed at 6.3-7.6ppm and 1.2-3.2ppm attributed to the aromatic protons and methylene and methine protons of the hyperbranched copolymer respectively. From the integration of the signals for the double bond and the aromatic protons respectively, and assuming that there is one double bond per hyperbranched copolymer macromolecule, the molar ratio of the double bond and the benzene rings was about 1:51 in this resulting copolymer. Considering the elemental analysis data of it at the same time, the molar ratio of the benzene rings and the nitrile groups was 51:26. The molecular weight of this resulting copolymer has been estimated at 9200, which is reasonable compared to the apparent Mn measured by multi-angle laser light scattering (9600).

The radical copolymerization of AN and PCMS took place smoothly. The time dependence of $\ln([M]_0/[M])$ was shown in Figure 4. The plot of $\ln([M]_0/[M])$ versus polymerization time appeared as a straight line, which indicated that the first order polymerization kinetics. This means that the concentration of propagating radical is constant during the polymerization.

Table 1 Characterization of resulting HP(PCMS-co-AN) and star-shaped HP(PCMS-co-AN)/PMMA

No.[d]	Time(h)	T(°C)	$\frac{[CuBr]}{[PCMS]_0}$	Con. of AN (%)	M_n[b]	M_w/M_n	Relative linearity (%)	$\frac{2^\circ-BCl}{1^\circ-BCl}$
1	12	60	0.04	6.88	2300	1.24	78.6	0.06
2	24	60	0.04	16.4	3100	1.26	72.4	0.08
3	36	60	0.04	33.2	4500	1.18	51.5	0.16
4	48	60	0.04	39.7	6500	1.09	47.1	0.18
5	24	66	0.04	27.6	2600	1.42	66.7	0.10
6	24	72	0.04	30.7	2300	1.88	53.8	0.15
7	24	60	0.02	10.1	1000	1.56	88.7	0.03
8	24	60	0.08	43.0	9600	2.26	40.8	0.21

a The polymerization condition: $[PCMS]_0=[AN]_0=2M$, CuBr:bipy=1:3, solvent: benzene

b Determined by a Waters 150 SEC apparatus, equipped with an Optilab DSP differential refractometer and a miniDAWN multi-angle (18-angles) laser light scatter detector (Wyatt Technology Co.) in THF with the wavelength λ= 690 nm

c The polydispersity indexes in Table 1 were lower than their ‘real’ values, because the low molecular weight species were removed in precipitation process[22]

d No.1~8: HP(PCMS-co-AN)$_{1\sim8}$

The information about the degree of branching

The degree of branching of the resulting hyperbranched copolymers was difficult to be determined directly and accurately by the integration of the broad signals in its 1H-NMR spectrum. However, the information about the degree of branching can be obtained in the relative linearity of the copolymers formed according to the method reported by J. M. J. Fréchet[9]. Because the branch points of the copolymer are same to that of hyperbranched poly[p-(chloromethyl)styrene], the ratio of the integration of the signals at 4.8ppm attributed to the secondary of benzylic chlorides (2°-BCl) to that at 4.5ppm attributed to the primary (1°-BCl) provides some useful information about the degree of branching. Although the ratio of 2°-BCl/1°-BCl is not a quantitative measure of the degree of branching, the smaller the ratio, the higher percentage of the relative linearity in the resulting hyperbranched polymer. On the other hand the percentage of the relative linearity in the hyperbranched polymer is higher, the degree of the branching is lower. In the case of the perfectly branched system, the ratio of the 2°-BCl/1°-BCl would be 0.5 and the percentage of relative linearity would be zero. In the extreme case where all but one of the benzylic chloride moieties are primary, the ratio of 2°-BCl/1°-BCl approaches zero, and the percentage of relative linearity would be 100%. From Table 1, the percentage of relative linearity in the resulting copolymers was from 48.8% to 88.7%, which displays the branched structure of them. The data in Table 1 also represented the effect on the degree of branching of the resulting hyperbranched copolymer in three ways: i) the polymerization temperature; ii) the molar ratio of catalyst to monomer; iii) the conversion. Unfortunately, the effect of temperature on the copolymerization is not easily explored because the rate of polymerization is slow below 50ºC and 78ºC is the boiling point of AN. In contrast, the influence of the catalyst (CuBr) concentration is more convenient to characterize. In one word, the higher are the temperature and the molar ratio of catalyst to monomer, the higher is the degree of branching of the given copolymer. This result is consistent with what Fréchet et al. reported for the polymerization of p-(chloromethyl)styrene by self-condensing atom transfer radical copolymerization[9]. Simultaneously, the effect of the conversion on the degree of branching was evident from the data of sample 1~4 in Table 1, the higher conversion, the higher degree of branching.

Effect of the molar fraction of AN in raw feed

In order to have a further insight into the structure of resulting copolymers, the atom transfer radical copolymerization of PCMS and AN with the CuBr/bipy catalyst at 60ºC at various molar fraction of AN in feed (f_{AN}) was performed. The data in Table 2 show the influence of f_{AN} on the molar fraction of AN in the copolymer (F_{AN}) and T_g of the resulting copolymers. As determined by elemental analysis, the change of f_{AN} (from 0.4 to 0.6) does not significantly alter the composition of the resulting copolymer and the F_{AN} is close to 1/3. The monomer reactivity ratios were evaluated by the Fineman-Ross method[23]. The value of monomer reactivity ratios can be obtained from the equation:

$$\frac{G_{AN}(g_{AN}-1)}{g_{AN}} = r_{AN}\frac{G_{AN}^2}{g_{AN}} - r_{PCMS} \qquad (\mathbf{1})$$

Here g_{AN} and G_{AN} were the molar ratio of AN/PCMS in raw feed and in copolymer respectively, which can be calculated from f_{AN} and F_{AN} in Table 2. r_{PCMS} was 0.937 and r_{AN} was 0.088. Then F_{AN} was calculated by the ideal composition equation including r_{PCMS} and r_{AN} and the results were also in Table 2. The calculated F_{AN} were approximate to the found F_{AN}. All copolymers displayed only one T_g by DSC measurement and the T_g of the copolymer was improved with increasing the content of AN in feed.

As well known, the copolymerization of CTC comonomers often leads to an alternative copolymer. For this reason, the ultraviolet spectrometer has been used to investigate whether PCMS and AN could form a CTC or not. However, no new absorbance signal has been found after mixing PCMS and AN in n-hexane, cyclohexanone or alcohol solution respectively. It may be too weak to be detected even if this kind of CTC exists[24,25]. The results in Table 2 illustrated that the CTC and the free monomer (PCMS) both participated in the atom transfer radical copolymerization of PCMS and AN [26-29], because r_{PCMS} was much larger than r_{AN}.

These copolymers possessed no ideal alternating structure in a large range of f_{AN}. If the amount of AN was in excess than that of PCMS in the feed, the predominantly alternating copolymer [PCMS-co-AN] could be obtained because no free monomer PCMS existed and they were all formed CTC with AN.

Table 2 Copolymerization Data for PCMS and AN at 60°C in benzene

f_{AN}	Element N Content in Copolymer (%)	F_{AN} (Found)	F_{AN} (Cal.)	Conversion of AN (%)	T_g(°C)
0.80	7.39	0.526	0.523	13.0	74.9
0.70	6.49	0.493	0.466	13.7	69.8
0.60	4.14	0.351	0.411	15.6	57.7
0.50	3.90	0.335	0.360	19.3	52.7
0.40	3.49	0.306	0.306	17.2	48.6
0.30	2.44	0.228	0.246	11.4	26.5

$[CuBr]:[bipy]:[M]_0=1:3:50$, $[M]_0=[PCMS]_0+[AN]_0=4M$, t=24h

Synthesis of Star-shaped Poly(PCMS-co-AN)/poly(MMA) Block Copolymer

In order to study the reactive activity of chlorine groups at the resulting hyperbranched copolymer ends, the sample HP(PCMS-co-AN)$_5$ was used as macroinitiator for ATRP of MMA in benzene. The ^{1}H-NMR spectrum of poly(PCMS-co-AN)$_5$/poly(MMA) was shown in Figure 5. The signals at 6.3-7.6ppm attributed to aromatic protons and the signals at 3.6ppm attributed to methoxyl protons preliminarily indicated the star-shaped structure of poly(PCMS-co-AN)$_5$/poly(MMA). The SEC curves of the HP(PCMS-co-AN)$_5$ and the poly(PCMS-co-AN)$_5$/poly(MMA) were presented in Figure 6. The SEC curve of the poly(PCMS-co-AN)$_5$/poly(MMA) showed only single peak as that of HP(PCMS-co-AN)$_5$, but the peak became much more wide and the retention time of the peak was decreased. These results further confirmed the HP(PCMS-co-AN)$_5$ as macroinitiator successfully initiated ATRP of MMA to form the star-shaped structure of poly(PCMS-co-AN)$_5$/poly(MMA) block copolymer.

Table 3 Characterization of Sample 5 and 9

Sample	Time (h)	T (°C)	M_n $\times 10^{-3}$	M_w/M_n
5	24	66	2.5	1.40
9	24	60	17.0	2.02

a. Determined by size exclusion chromatography (SEC) (Waters 150, USA) equipped with single RI detector (Waters 410), calibrated universally by linear polystyrene standards, THF as the eluent with a flow rate of 1ml/min
b. The polydispersity indexes in Table 3 were lower than their 'real' values, because the low molecular weight species were removed in precipitation process[22]
c. No.9: star-shaped poly(PCMS-co-AN)$_5$/poly(MMA)

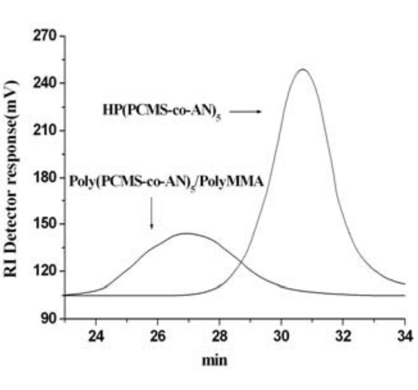


Figure 6 The SEC curves of HP(PCMS-co-AN)$_5$ and star-shaped poly(PCMS-co-AN)$_5$/poly(MMA)

According to Figure 5, the signals at 4.5-4.8ppm attributed to the methylene protons adjacent to chlorine atoms (1º-BCl) that was not able to initiate MMA to polymerize. From the ratio of the peak area of the signals at 6.3-7.6ppm attributed to the aromatic protons and that of the signals at 4.5-4.8ppm in the 1H-NMR spectra of the HP(PCMS-co-AN)$_5$ and the star-shaped poly(PCMS-co-AN)$_5$/poly(MMA), it can be concluded that about 60% chlorine atoms adjacent to HP(PCMS-co-AN)$_5$ (i.e. seven chlorine atoms per core) initiated MMA to form PMMA arms. By integration of the peak area at 3.6 ppm (attributed to the methoxyl protons) and assuming that there is only one 3º-BCl per arm, the average length of each arm of the star-shaped block copolymer is about 20 units of MMA. On the other hand, the average length of each arm of the star-shaped block copolymer can also be calculated from the molecular weights of the HP(PCMS-co-AN)$_5$ and the star-shaped poly(PCMS-co-AN)$_5$/poly(MMA) in Table 3. The two results consisted with each other.

Conlusions

In a conclusion, a series of novel hyperbranched copolymers have been successfully synthesized from PCMS and AN by the CTC and the SCVP. The results indicated that copolymerization process was controllable and possessed a “living” polymerization. The predominantly hyperbranched alternating copolymers HP(PCMS-co-AN) can be obtained only when the amount of AN was in excess than that of PCMS in the feed. These hyperbranched alternating copolymers can be further used as macroinitiator to prepare the star-shaped poly(PCMS-co-AN)/poly(MMA).

Acknowledgement We thank Dr. Gao Chao for kind and helpful discussion.

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