Preparation of Poly(acrylamide) with Configurational Sequences by Photo Living Polymerization

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Poly(acrylamide) (PAM) with configurational sequences was synthesized under ultraviolet (UV) catalyzed by Lewis acid (here yttrium salts) and in the presence of dibenzyl trithiocarbonate (DBTTC). DBTTC is selected as the photoinitiator and also the chain-transfer agent to achieve a living manner for the polymerization process. A series of PAMs with narrow molecular weight distributions and different configurational sequences have been prepared. The catalysis effects on configurational control of different contents of the yttrium salts have been studied.

The properties of the polymeric materials are often greatly affected by the stereo-regularities of the main chain, while controlled/living radical polymerization (CRP) techniques allow the synthesis of well-defined (co)polymers with controlled degrees of polymerization and low molecular-weight distributions.[1]

In this paper, we report a new method for preparation of PAMs with well-defined configurational sequences and narrow molecular-weight distributions by CRP in the presence of $Y(OTf)_3$ (OTF: trifluoromethanesulfonate). The polymerization is performed in methanol at 40 °C in the presence of DBTTC under UV and characterized by GPC and ^{13}C NMR.

Under UV irradiation, the "C–S" bond in DBTTC between benzyl group and sulfur is broken, and the generated benzyl radicals can initiate the polymerization of AM monomers. The propagating radical can transfer towards the trithiocarbonate radical and form a dormant polymer chain. The fast equilibrium between propagating chain radical and dormant species controls the polymerization in a living manner.[2] In free radical polymerization of AM monomers without Lewis acid, the sp^2 hybridized carbon radical has a nearly planar configuration, which offers almost the same possibility for both "meso" (m) or "racemo" (r) additions.[3] However, the coordination of Lewis acid, such as $Y(OTf)_3$, with the last two units of a growing PAM chain can force them into the "meso" configuration during monomer addition.[4] In that case, the nature of the coordination functional group "—$CONH_2$" is the predominant parameter for the stereocontrol. For acrylamide, this complexation leads to polymers with the configurational sequences containing more "meso" content.

Methanol (AR) was purchased from Shanghai Zhenxin Chemical factory and used as received. AM monomers were recrystallized from ethyl acetate, then filtered and dried before the polymerization. The yttrium salts ($Y(OTf)_3$ were prepared according to the published procedures.[5] DBTTC was also synthesized according to the process in the reference.[6] The ^{13}C NMR spectra were recorded on a Bruker WH 400 spectrometer. The general condition of the measurements is as follow: The polymer concentration in D_2O solution is about 15% by weight. The proton-decoupled ^{13}C NMR spectra were obtained at 100.62 MHz and 70 °C. The pulse width is 30 µs (corresponding to a flip angle of 60°) and an acquisition time (and pulse interval) of 0.8 s were used. The molecular weight and molecular weight distributions of PAMs were obtained on a PE200 GPC instrument at 25 °C. 0.01 M $NaNO_3$ aqueous solution was chosen as the eluent with the flow rate of 1.0 mL/min. PEO standards are chosen for the GPC calibration.

A general procedure for the photo polymerization is described as follows: designated amounts of $Y(OTf)_3$ and DBTTC were added into a glass polymerization tube, then a solution of AM in degassed methanol (monomer concentration = 4.5 M) was introduced. The mixture was stirred for 5 min at room temperature in order to dissolve the yttrium salt. The glass tube was thoroughly deoxidized by alternate vacuum and nitrogen flush for at least 3 times and then sealed with pure nitrogen gas inside. The tube was then placed at a distance of 10 cm to a broadband mercury UV lamp (main wavelength 365 nm, 125 W). The detected real temperature of polymerization was 40 °C. The reaction system was polymerized with stirring for a certain session and stopped by shutting down the UV lamp. The mixture of products was dissolved in H_2O and then precipitated into ethanol and dried in high vacuum at 50 °C till constant weight.

Figure 1 shows the ^{13}C NMR spectrum of PAM prepared by photopolymerization at 40 °C with the therapy of [AM]/[catalyst]/[DBTTC] = 500/0/1. It shows that a fine band splitting occurs in the 100.62 MHz ^{13}C NMR spectrum, which indicates the existence of various configurational structures.[7] The NMR curve with overlapped peaks can be further divided into pentad sequences proposed by Lancaster and O'Connor.[8] In D_2O solutions the resonances of the pentad sequences partly overlap, which prevents the quantitative determination of pentad structures in the polymer chain by direct integration of the curves in the ^{13}C NMR spectrum. The NMR curve can be fitted by Gaussian/Lorentzian lines, which permits a division of the

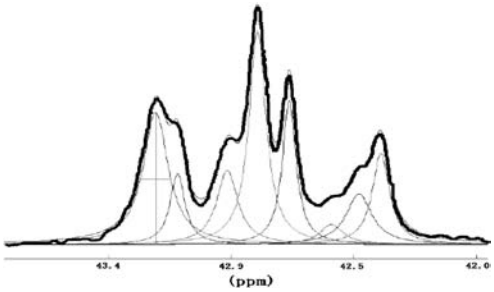

Figure 1. Typical ^{13}C NMR spectrum and the Gaussian/Lorentzian line fit.

Table 1. Proportion of pentad sequences (%): the effects of different $Y(OTf)_3$ contents

Chemical Shift	Assign	[AM]:[DBTTC]:[Y(OTf)$_3$]			
		500:1:0	500:1:18	500:1:25	500:1:50
42.42	[mmmr]	10.63	8.90	7.37	8.94
42.50	[rmmr]	8.76	8.88	13.62	12.04
42.59	[mmmm]	3.17	9.01	12.86	29.97
Σ_{mm}[a]		22.56	26.79	33.85	50.95
42.72	[rmrr]	13.16	8.19	5.62	0.91
42.84	[mmrr] + [rmrm]	24.28	22.81	22.38	18.14
42.96	[mmrm]	10.58	15.90	15.37	19.69
Σ_{mr}		48.02	46.90	43.37	38.74
43.12	[rrrr]	7.09	1.88	0.63	6.27
43.21	[rrrm] + [mrrm]	22.33	24.43	22.15	4.04
Σ_{rr}		29.42	26.31	22.78	10.31
$P_m = \Sigma_{mm} + 0.5\Sigma_{mr}$		46.57	50.24	55.54	70.32
M_n, GPC $\times 10^{-4}$		2.71	4.01	4.50	5.06
M_w/M_n		1.17	1.22	1.25	1.24

[a] The sums are based on the assumption of the Bernoullian statistics.

overlapped peaks.[9] By the Gaussian/Lorentzian fit with the peak widths adjusted to give a close match to the experimental trace, quantitative determination of pentad populations in the polymer chain can be carried out by quantitative integration of detached peaks. The "meso" dyad probability is calculated by the data of pentads assuming the Bernoullian statistics.[10]

Table 1 shows the production of PAMs with different configurational sequences prepared with different $[Y(OTf)_3]/[AM]$ ratios and the molecular weight as well as the molecular weight distributions. The narrow molecular weight distributions indicate that the polymerization is in a living/controlled manner, and the meso dyads content (P_m) shows an increase with the increase of original concentration of $Y(OTf)_3$. Furthermore, the addition of $Y(OTf)_3$ can accelerate the polymerization in a manner similar to the report for the methacrylates.[11] The polymerization with Lewis acid catalyst $Y(OTf)_3$ ($[AM]:[DBTTC]:[Y(OTf)_3] = 500:1:50$, at 40 °C) produced a yield of 86% within 6 h, while without $Y(OTf)_3$ at the same condition can only get 50% conversion over 8 h. However, more Lewis acid results in a broader molecular weight distribution, for example, $[AM]/[DBTTC]/[Y(OTf)_3] = 500:1:0$, conversion = 47%, PDI = 1.17; $[AM]/[DBTTC]/[Y(OTf)_3] = 500:1:65$, conversion = 89%, PDI = 1.50. This can be caused by both the loss of living nature since a higher speed of chain propagation and a slight degradation of DBTTC or macro-trithiocarbonate in the presence of Lewis acid.[12]

Figure 2 shows a first-order plot of meso dyads content with respect to $[Y(OTf)_3]/[AM]$ ratios, which indicates a constant complexation number of AM with $Y(OTf)_3$ by coordination.

From the slope of Figure 2 it can be calculated that the "meso" dyads content increases roughly 2.05% with an increment of 0.01 of the $[Y(OTf)_3]/[AM]$ ratio, which implies that a constant proportion of the coordination take part in the "meso" addition control.

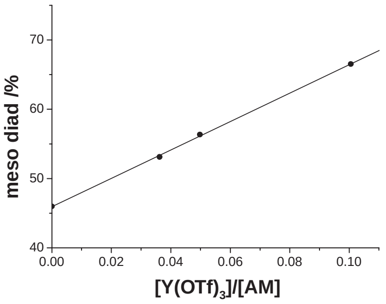

Figure 2. Relationship between the dyad contens of PAM and the initial $[Y(OTf)_3]/[AM]$ ratios.

In conclusion, a new method has been developed for preparation of PAMs with well-defined configurational sequences and narrow molecular-weight distributions by photo living polymerization in the presence of DBTTC and catalyzed by yttrium salts. Well-defined PAMs with narrow molecular weight distributions and different configurational sequences were synthesized successfully. The $[Y(OTf)_3]/[AM]$ ratio affects the configurational sequences as well as the total content of meso dyads in the final composition of PAMs. The introduction of Lewis acid accelerates the polymerization but results in a broadening of the molecular weight distribution. In a certain polymerization system, the "meso" composition of the prepared PAM increases linearly with the initial $[Y(OTf)_3]/[AM]$ ratios.

References

1 *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT*, ed. by K. Matyjaszewski, ACS Symp. Ser., **2000**.

2 R.-K. Bai, Y.-Z. You, C.-Y. Pan, *Macromol. Rapid Commun.* **2001**, *22*, 315.

3 J. Lutz, D. Neugebauer, K. Matyjaszewski, *J. Am. Chem. Soc.* **2003**, *125*, 6986.

4 a) V. Coessens, T. Pintauer, K. Matyjaszewski, *Prog. Polym. Sci.* **2001**, *26*, 337. b) Y. Isobe, D. Fujioka, S. Habaue, Y. Okamoto, *J. Am. Chem. Soc.* **2001**, *123*, 7180.

5 a) S. Kobayashi, I. Hachiya, M. Araki, H. Ishitani, *Tetrahedron Lett.* **1993**, *34*, 3755. b) M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1675.

6 B. Tamami, A. R. Kiasat, *J. Chem. Res. (S)* **1998**, 454.

7 J. Spěváček, M. Suchopárek, S. Al-Alawi, *Polymer* **1995**, *36*, 4125.

8 J. E. Lancaster, M. N. O'Connor, *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 547.

9 G. Maurin, P. Senet, S. Devautour, P. Gaveau, F. Henn, V. E. Van Doren, J. C. Giuntini, *J. Phys. Chem. B* **2001**, *105*, 9157.

10 *Comprehensive Polymer Science*, ed. by A. Geoffrey, Pergamon Press, **1989**.

11 E. L. Madruga, J. S. Roman, M. J. Rodriguez, *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2749.

12 a) D. B. Thomas, A. J. Convertine, L. J. Myrick, C. W. Scales, A. E. Smith, A. B. Lowe, Y. A. Vasilieva, N. Ayres, C. L. McCormick, *Macromolecules* **2004**, *37*, 8941. b) J. F. Lutz, W. Jakubowski, K. Matyjaszewski, *Macromol. Rapid Commun.* **2004**, *25*, 486.

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