Polymer Bulletin 43, 29–34 (1999)

Polymer Bulletin

Self-condensing vinyl polymerization of acrylamide

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Received: 8 January 1999/Revised version: 26 May 1999/Accepted: 25 June 1999

Summary

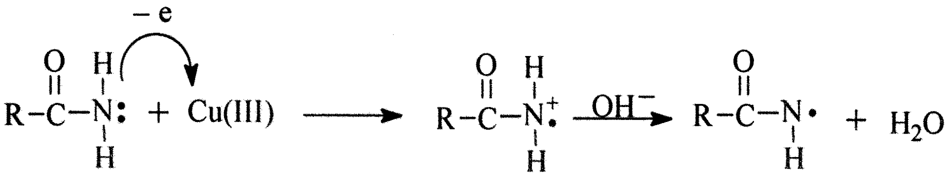
A novel approach to branched polyacrylamide was described. The branched structure resulted from the amidyl radicals which were formed by the reaction of amide groups with Cu(III) of potassium diperiodatocuprate, $K_5[Cu(HIO_6)_2]$, in alkaline medium and capable of initiating the vinyl polymerization of acrylamide monomer. The obtained polymer was characterized by ^{1}H NMR, FT-IR and intrinsic viscosity measurements.

Introduction

Dendritic macromolecules have been under intense investigations (1), (2). They can be divided into two kinds: dendrimers and hyperbranched polymers. Hyperbranched polymers by one-pot polymerization are readily available in view of application. Although they are structurally less perfect than regularly branched dendrimers, hyperbranched polymers have been extensively studied because they might use commercially available monomers to produce highly branched structures in a limited numbers of steps. Flory (3) first suggested the possibility of forming hyperbranched polymers by direct one-pot polymerization of AB_n type monomers, where $n \geq 2$ and functional group A can react with B. For example, hyperbranched aliphatic esters (4) and phenylenes (5) have been prepared.

Fréhet et al. (6) reported an alternative route, i.e. self-condensing vinyl polymerization, to hyperbranched polymers. In the process described by Fréchet, an AB vinyl monomer with a B group that may be activated by an external stimulus to a B^* moiety that itself is capable of initiating the polymerization of a vinyl monomer. According to this idea, Matyjaszewski et al. (7) prepared hyperbranched polystyrene by one-pot, atom transfer radical polymerization using *p*-(chloromethyl)styrene in the presence of CuCl and 2,2'-bipyridyl.

Liu et al. (8) reported acrylamide polymerization which was initiated by Cu(III) of potassium diperiodatocuprate, $K_5[Cu(HIO_6)_2]$ (9), in alkaline medium. According to Nikishin's results (10), Liu et al. suggested the mechanism of initiation as follows:



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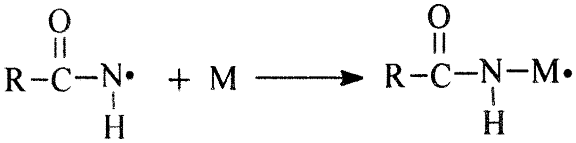


The mechanism of initiation involves one-electron oxidation of an amide to an amidyl radical by means of Cu(III). One electron of the nitrogen atom is abstracted by Cu(III) to form a cation radical. The cation radical subsequently loses a proton in alkaline medium, resulting in an amidyl radical which is capable of initiating the vinyl polymerization of acrylamide. The concentration of initiator used by Liu et al. was very small and the high molecular weight polymer was obtained.

This initiation mechanism is basically in agreement with the idea of self-condensing vinyl polymerization. The branched structure might be formed when the concentration of the initiator was increased. Furthermore, the branched structure is generated at the nitrogen atom, which has not been reported previously. In this work, we describe the preparation of the branched polyacrylamide by one-pot polymerization using Cu(III) initiator.

Experimental part

Preparation

The Cu(III) solution was prepared according to the literature (11). $CuSO_4 \cdot 5H_2O$ (3.54 g), KIO_4 (6.82 g), $K_2S_2O_8$ (2.20 g) and KOH (9.00 g) were added to about 200 ml of distilled water. The mixture was refluxed for 40 minutes. After cooling to the room temperature, the mixture was filtered and the filtrate was diluted to 250 ml with distilled water. The final concentration of Cu(III) was titrated as 0.056M.

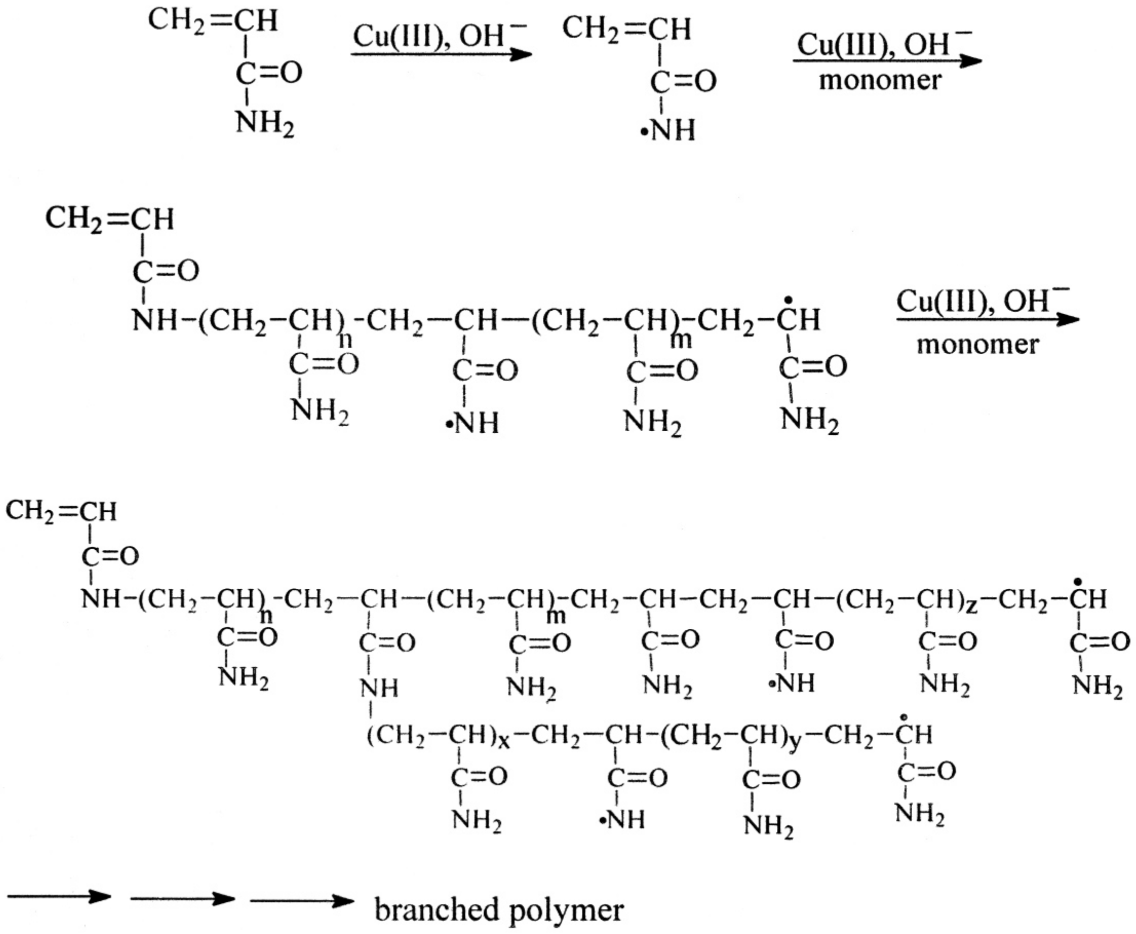
An appropriate amount of monomer was added to the Cu(III) solution. The polymerization was carried out at 40°C under nitrogen atmosphere. After the completion of polymerization, the reaction mixture was filtered. The pH of the polymer solution was adjusted to 6-7 by addition of hydrochloric acid. The precipitation formed was filtered out and the solution was concentrated and poured into methanol. The resulting polymer was dried under vacuum at 50°C for two days.

Characterization

^1H NMR spectra were recorded on a Varian 300MHz spectrometer with D_2O as solvent. IR spectra were obtained on a Perkin-Elmer model 2000 FT-IR spectrophotometer. The compounds were sampled on KBr plates. Intrinsic viscosity measurements were made at 25°C with distilled water as the solvent in a Ubbelohde dilution viscometer having a negligibly small kinetic energy correction.

Results and discussion

Scheme 1. Schematic of the Polymerization of Acrylamide by Self-condensing Vinyl Polymerization to Form a Branched Polymer



Scheme 1 outlines the formation of branched polyacrylamide by self-condensing vinyl polymerization. The amide group of the acrylamide monomer can be activated by Cu(III) with redox reaction to form an amidyl radical which is capable of initiating the polymerization of acrylamide to result in a linear polymer. Meanwhile, the new initiating centers of amidyl radicals might be formed at the pendant amide groups of the obtained polyacrylamide and lead to the formation of branched structure. The mechanism of polymerization is in agreement with Fréchet's idea. Nevertheless, in our case, the proton adjacent to the nitrogen atom loses in alkaline medium and, in Fréchet's and Matyjaszewski's cases, the chlorine atom at the benzylic position dose not lose and is still contained in the final polymer.

Table 1. Polymerization of acrylamide initiated by Cu(III) at 40°C

Polymer No.	Monomer (g)	Cu(III) solution (ml)	mol. ratio of Cu(III) to monomer	reaction time (h)	yield (%)	[η] (dl/g)
A	0.5	1.25	0.01	24	97	3.677
B	0.5	5.0	0.04	48	96	2.111
C	2.0	50	0.10	24	45	1.567
D	1.0	50	0.20	48	92	0.691
E	1.2	90	0.30	48	90	0.387

Table 1 lists the results obtained by polymerization of acrylamide by self-condensing vinyl polymerization. From Table 1, it can be seen that the intrinsic viscosity obviously decreases from polymer A to polymer E. This result could be attributed to the increase of the ratio of initiator to monomer and also to the formation of the branched structure and the raise of the degree of branching.

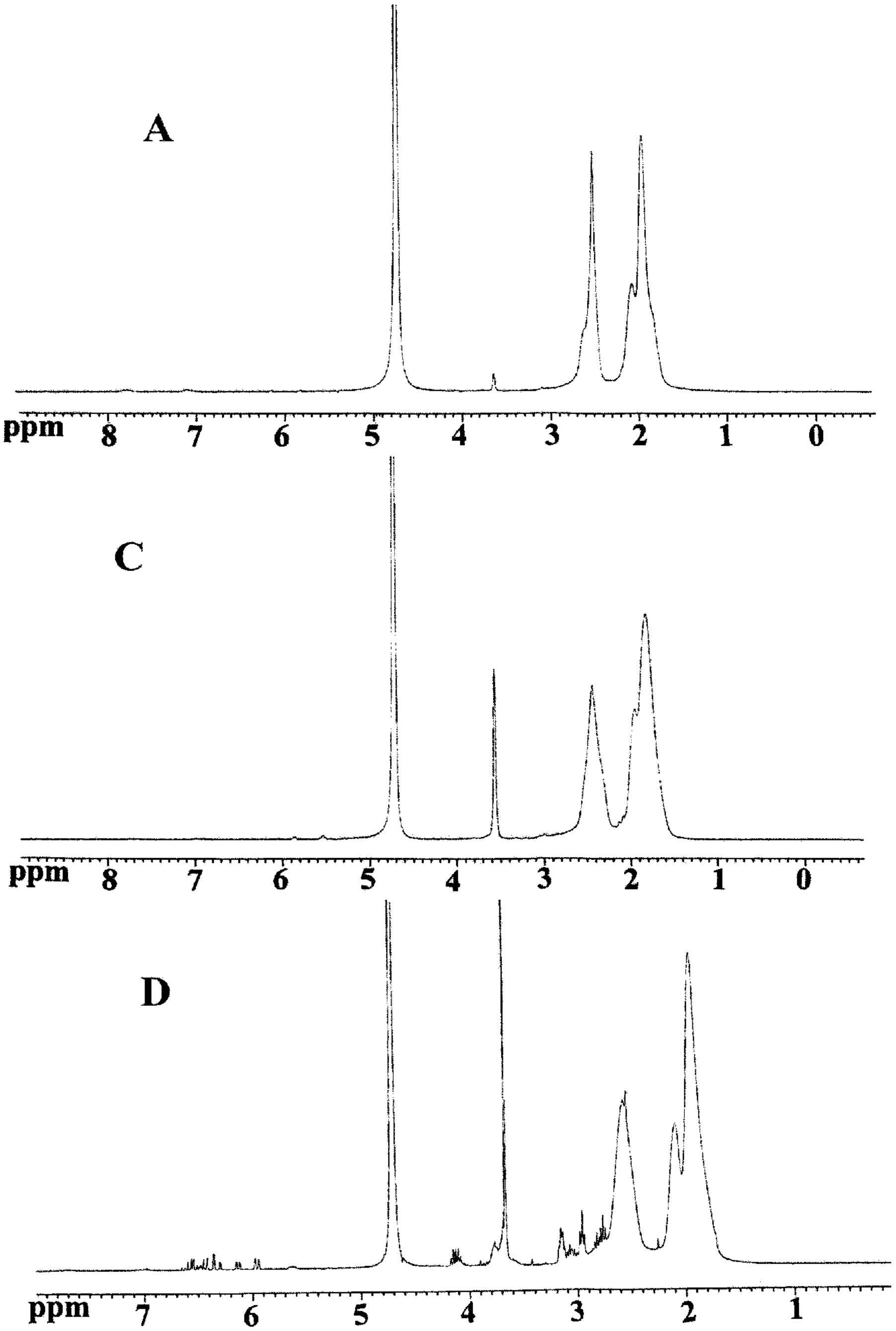


Figure 1. ^1H NMR 300MHz spectra of polyacrylamide A, C and D in D_2O

The formation of the branched structure might be confirmed by the ^1H NMR measurements (Figure 1). The signal at 1.8 ppm arises from the two methylene protons of main chain and the methine proton absorbs at 2.3 ppm. The signal at 3.6 ppm is due to the two methylene protons adjacent to the nitrogen atom and increases with the increase of the initiator used. The ratio of the integration of this signal to that of two methylene protons of main chain provides some information to estimate the degree of branching. The experimentally observed ratios for polymer A, C and D are about 1:66, 1:9 and 1:6, respectively. For a perfect branched structure, i.e., each polymerized acrylamide unit can be activated to form two kinds of radicals (amidyl radical and carbon radical), the ratio might be considered to be 1:1. This indicates that the obtained polyacrylamide possesses a partly branched structure.

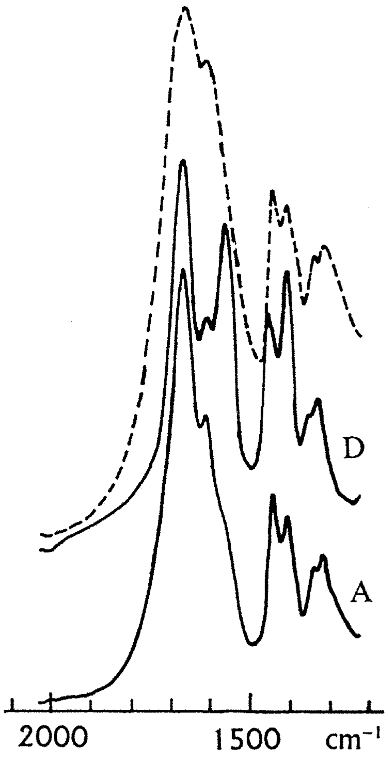


Figure 2. FT-IR spectra of polyacrylamide
---- linear polyacrylamide;
A: branched polyacrylamide A; D: branched polyacrylamide D

The branched structure also can be observed by the FT-IR measurements (Figure 2). A typical linear polyacrylamide shows the characteristic absorption of the primary amide at 1666 cm^{-1} for C=O stretch and 1608 cm^{-1} for N-H bending in IR spectra (dash curve in Figure 2). Bassignana et al. (12) compared the IR features of polyacrylamide and N-mono-substituted polyacrylamide, and suggested that the N-H bending of the secondary amide in the N-mono-substituted polyacrylamide absorbed near 1560 cm^{-1} and the linear polyacrylamide did not have this absorption. In the case of branched polyacrylamide A, there is a slight shoulder in IR spectrum around 1560 cm^{-1}, which implies only little amount of secondary amide structure, i.e. branched structure, in the polymer. For polyacrylamide D, besides the absorption of C=O and N-H of the primary amide, the strong peak at 1566 cm^{-1} shows that there exists the secondary amide in the obtained polymer and the branched structure is generated at the nitrogen atom.

References

1. Tomalia DA, Naylor AM, Goddard III WA (1990) Angew Chem Int Ed Engl 29: 138
2. Matthews OA, Shipway AN, Stoddart JF (1998) Prog Polym Sci 23: 1
3. Flory PJ (1952) J Am Chem Soc 74: 2718
4. Hult A, Malmstron E, Johansson M (1993) J Polym Sci: Polym Chem Ed 31: 619
5. Kim YH, Webster OW (1992) Macromolecules 25: 5561
6. Fréchet JMJ, Henmi M, Gitsov I, Aoshima S, Leudc M, Grubbs RB (1995) Science 269: 1080
7. Gaynor SG, Edelman S, Matyjaszewski K (1996) Macromolecules 29: 1079
8. Liu YH, Song XR, Shi HM, Xu LL (1990) Chemical Journal of Chinese Universities (Chinese Edition) 11: 328
9. Balikungeri A, Pelletier M, Monnier D (1977) Inorg Chim Acta 22: 7
10. Nikishin GI, Svitanko IV, Troyansky EI (1983) J Chem Soc Perkin Trans II 5: 595
11. Jaiswal PK, Yadava KL (1973) Indian J Chem 11: 837
12. Bassignana P, Cogrossi C, Polla-Mattiot G (1963) Spectrochimica Acta 19: 2129