

反相微乳液中疏水缔合型聚丙烯酰胺的合成及其性能研究*

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摘 要 在反相微乳液体系中合成了疏水缔合型聚丙烯酰胺(HAPAM),用 Brookfield 旋转粘度计测定了其水溶液性能,并与传统胶束聚合法制备的 HAPAM 作了比较.结果显示,前者有更优越的耐盐和抗剪切性能,这主要是因为前者的大分子链上疏水共聚单体呈无规分布而后者呈嵌段分布,其疏水分子链以分子间而不是分子内缔合为主.

关键词 疏水缔合,反相微乳液,聚丙烯酰胺,表观粘度

疏水缔合型水溶性聚合物(Hydrophobically associating water-soluble polymers)是亲水性大分子链上带有少量疏水基团的水溶性聚合物^[1].由于表现出与高分子量聚合物一样的表观粘度,而且具有更好的耐盐性和抗剪切性,因此,近年来疏水缔合型水溶性聚合物作为流度控制剂、强化采油剂、涂料增稠剂和絮凝剂等得到广泛应用^[2~4],已引起人们的极大关注和兴趣.但是,对于这类聚合物的合成,一般来说很难用普通方法完成,因为油性单体和水溶性单体极性差别大,难以充分混合.迄今为止,文献报道的合成方法大多仅限于胶束聚合法^[5],本文用反相微乳液聚合法制备了疏水缔合型聚丙烯酰胺(HAPAM),测定了其水溶液性质,分析了各种影响因素,并与传统的胶束聚合法制得的产物作了分析比较.

1 实验部分

1.1 原料

所用试剂均为化学纯和分析纯.

1.2 疏水缔合型聚丙烯酰胺(HAPAM)的合成

1.2.1 胶束共聚合法 在 1L 反应瓶中加入 500mL 去离子水,15g 十二烷基硫酸钠,0.4~1.6g 丙烯酸十二烷基聚氧乙烯醚(3)酯(DEAE),搅拌溶解,随后加 30g 丙烯酰胺搅拌溶解,通氮 30min,在 $32 \pm 1^\circ\text{C}$ 水浴温度下加入 0.018g 过硫酸铵和 0.15g 尿素引发聚合,待放热高峰过去后,保温搅拌反应 4h,出料.将所得粗产物稀释溶解,

用丙酮沉淀,洗涤,抽提,除去残留单体、胶束化剂及水分.在 50°C 下真空干燥 5h,将所得精制产物置于干燥器中备用.

1.2.2 反相微乳液共聚法 在 250mL 反应瓶中,保持水浴温度为 $32 \pm 1^\circ\text{C}$,加入 90mL 200# 溶剂油,12g 二异辛基磷酸钠,0.4~1.5g 丙烯酸十二烷基聚氧乙烯醚(3)酯,搅拌溶解,随后滴入 60mL 40% 丙烯酰胺水溶液,搅拌乳化使之形成微乳液,通氮驱氧 30min,然后加入 300 μL 过氧化二碳酸二异辛酯引发聚合,保温反应 6h,出料.粗产物精制同上.

1.3 聚合物水溶液表观粘度的测定

定量称取精制后的聚合物溶于水或盐水中,稀释配成溶液,自然放置 7 天,待其完全溶解后,用 Brookfield 粘度计测定粘度.聚合配方及产物溶解性列于表 1.

Table 1 Reaction recipe and product solubility

Sample	Co-monomer content (mol %)	Preparation method	Conversion (%)	Solubility
PAM(I)	0	I	87.6	Soluble
HAPAM(I-0.25)	0.25	I	87.1	Soluble
HAPAM(I-0.5)	0.5	I	89.0	Soluble
HAPAM(I-0.75)	0.75	I	88.2	Soluble
HAPAM(I-1)	1	I	89.4	Soluble
PAM(II)	0	II	91.3	Soluble
HAPAM(II-0.25)	0.25	II	93.5	Soluble
HAPAM(II-0.5)	0.5	II	92.7	Soluble
HAPAM(II-0.75)	0.75	II	91.2	Soluble
HAPAM(II-1)	1	II	93.0	Insoluble

I: Micelle polymerization; II: Inverse microemulsion polymerization

2 结果与讨论

2.1 聚合物浓度对水溶液表观粘度的影响

图 1 和图 2 分别在 0.342mol/L NaCl 水溶液及纯水中,反相微乳液聚合法制得的产物表观粘度与聚合物浓度的关系曲线.由图 1 和图 2 可见,AM 均聚物水溶液的表观粘度随聚合物浓度的增加而有所增加,但幅度不大,而通过反相微乳液聚合法制得的共聚物,其水溶液的表观粘度随聚合物浓度的增加而持续增加.从图 1,2 还可以看到,在相同条件下,共聚单体的含量越多,其共聚物水溶液表观粘度也越大,即使在低聚合物浓度区间内也如此. DEAE 含量为 0.75mol% 时,共聚物水溶液表观粘度最大,因而在图中其曲线位置最

高,其次是含量为 0.5% (mol) 的共聚物,再次为 DEAE 含量 0.25% (mol),这表明,AM 大分子链上疏水性共聚单体的加入,使大分子链团间产生疏水缔合,形成了物理交联网络,从而提高了水溶液的表观粘度^[6]. 这种作用效果随着疏水性共聚单体含量的增加而增加,也随着共聚物浓度的增加而增加. 图 3 为用胶束聚合法制得的疏水缔合共聚物,其盐水溶液表观粘度与聚合物浓度的关系曲线.从图中可以看到,当共聚单体(DEAE)含量为 0.25% 时,其水溶液粘度基本上没有什么变化,与均聚物的几乎一致,但以后,随 DEAE 含量的增加,共聚物水溶液的表观粘度也增大.从图 3 中还可以看到两个现象:(1)DEAE 含量为 1% 时,其水溶液粘度反而下降至低于含量为 0.5% 的共聚物水溶液表观粘度;(2)DEAE 含量为 0.5% 和 0.75% 的两种共聚物随聚合物浓度增加而增加的幅度较大,在超过 0.2g/dL 后更是急剧增加,可以把 0.2g/dL 视为表观粘度增加的临界浓度值.

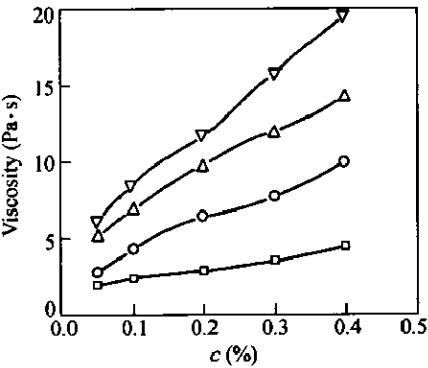


Fig. 1 Effect of polymer concentration on its apparent viscosity in 0.342mol/L NaCl solution at 25°C and a shear rate of 1.3 s⁻¹
PAM(Ⅱ)(□); HAPAM(Ⅱ-0.25)(○); HAPAM(Ⅱ-0.5)(△); HAPAM(Ⅱ-0.75)(▽)

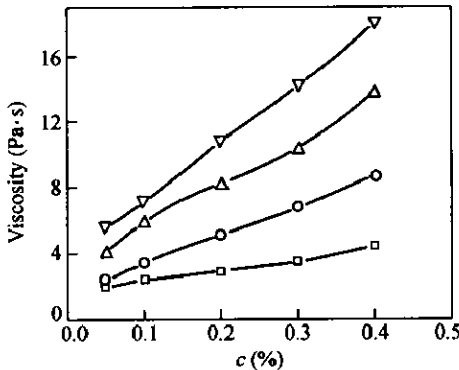


Fig. 2 Effect of polymer concentration on its apparent viscosity at 25°C and a shear rate of 1.3 s⁻¹
PAM(Ⅱ)(□); HAPAM(Ⅱ-0.25)(○); HAPAM(Ⅱ-0.5)(△); HAPAM(Ⅱ-0.75)(▽)

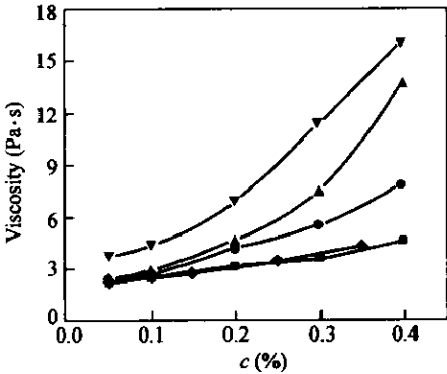


Fig. 3 Effect of polymer concentration on its apparent viscosity in 0.342mol/L NaCl solution at 25°C and a shear rate of 1.3 s⁻¹
PAM(Ⅰ)(□); HAPAM(Ⅰ-0.25)(◇); HAPAM(Ⅰ-0.5)(△); HAPAM(Ⅰ-0.75)(▽); HAPAM(Ⅰ-1)(○)

从以上对图 1、图 2 和图 3 的比较分析可以看到,用反相微乳液聚合法与用胶束聚合法所制得的疏水缔合型共聚物,其水溶液性质有显著的不同.胶束聚合基本上类似于水溶液聚合,即水溶性引发剂在水溶液中引发丙烯酰胺的聚合.所不同的是,胶束聚合时水溶液中还存在有由 SDS 组成的胶束,胶束内核还包有油溶性的共聚单体.聚合开始后,丙烯酰胺单体在水溶液中聚合,而油性单体以微胶束形式参与共聚,结果生成了嵌段

共聚物,共聚单体以嵌段的形式分布在大分子主链上^[7].而在反相微乳液聚合法中,共聚单体具有一定的表面活性,大部分分布在油水界面上的乳化剂层内,丙烯酰胺单体也有一定的助乳化作用,有少部分也会分布在乳化剂层内.油溶性的引发剂生成初级自由基后,在乳化剂层内同时引发丙烯酰胺和共聚单体的聚合,它们可以发生无规共聚,结果生成了无规的共聚物而不象胶束聚合法那样生成嵌段共聚物.疏水单体呈无规分布的PAM主链,在水溶液中容易形成分子链与分子链间的缔合,而疏水单体呈嵌段分布在PAM主链上,存在有分子间和分子内两种疏水缔合的竞争^[8].对于HAPAM(I)来说,在疏水基团含量较低的情况下,随疏水基团含量增加,分子链上疏水嵌段长度增加,疏水缔合增强,溶液粘度增大;当疏水嵌段长度继续增加时,疏水嵌段的自身缔合趋势增大,更有利于分子内缔合,导致粘度随疏水基团含量增加而降低.而聚合物浓度的增加则有利于分子间的疏水缔合,在0.2g/dL左右,分子间的疏水缔合迅速增加,这就是HAPAM(I-0.5),HAPAM(I-0.75)存在着粘度跃升的临界值的原因.

2.2 温度对共聚物水溶液表现粘度的影响

0.3g/dL的共聚物HAPAM(II-0.5)的水溶液在剪切速率为 $1.3s^{-1}$ 时,其表现粘度与温度的关系如图4所示.由图可见,随着温度的升高,共聚物水溶液的表现粘度下降这是因为温度的升高,使得疏水基团的热运动加剧,疏水缔合作用被大大削弱,共聚物水溶液的粘温关系表现为常见的粘温关系.

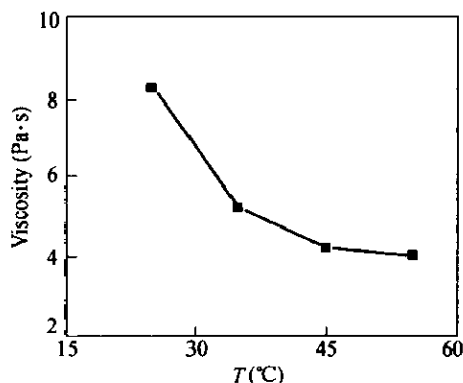


Fig. 4 Effects of temperature on the apparent viscosity of HAPAM(II-0.5) a shear rate of $1.3s^{-1}$ and a copolymer concentration of 0.2g/dL

2.3 电解质水溶液对共聚物水溶液表现粘度的影响

不同离子强度的NaCl和CaCl₂电解质浓度对溶液表现粘度的影响如图5所示.电解质浓度增大时,作为溶剂的水的极性增强,使疏水基团之间的缔合作用加强,大分子线团物理交联点增多,因而溶液粘度升高.相比之下,AM均聚物溶液粘度不随盐浓度的增加而变化,因为其分子链间不存在疏水基团的缔合作用.可见,所制得的疏水共聚物具有良好的耐盐能力.

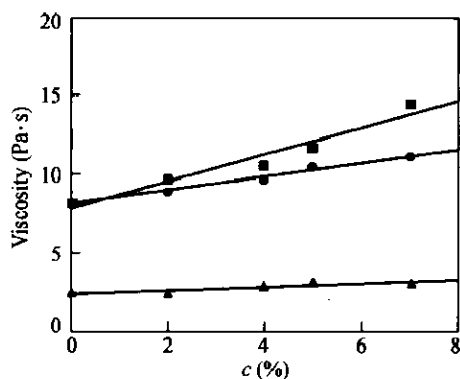


Fig. 5 Effect of ionic strength of NaCl and CaCl₂ solutions on the apparent viscosity of HAPAM(II-0.5) at 25°C, a shear rate of $1.3s^{-1}$ and a copolymer concentration of 0.2g/dL
NaCl(●); CaCl₂(■); PAM(II)(▲)

2.4 表面活性剂对共聚物水溶液表现粘度的影响

用HAPAM(II-0.5)共聚物考察了阴离子表面活性剂十二烷基硫酸钠(SDS)和非离子表面活性剂十二醇聚氧乙烯醚(3)(DE)对其水溶液粘度

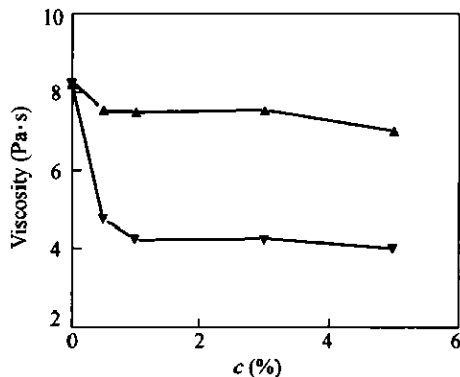


Fig. 6 Effect of surfactant concentration on apparent viscosity of HAPAM(II-0.5) at 25°C, a shear rate of $1.3s^{-1}$ and a copolymer concentration of 0.2g/dL
SDS(▲); DE(▼)

的影响,如图 6 所示.从图中可以看到,SDS 与 DE 对共聚物水溶液表观粘度的影响有很大的不同. SDS 浓度的增加,使共聚物水溶液表观粘度下降,但下降幅度并不大,用少量的 DE(0.5g/dL)就使表观粘度迅速下降.前面已提到,疏水缔合型共聚物,其水溶液表观粘度很大程度上是由十二烷基聚氧乙烯醚侧链相互缔合作用提供的.当加入小

分子十二醇聚氧乙烯醚(3)时,由于结构相似,DE 很容易进入疏水缔合区域,起到了一种润滑作用,使分子链间的十二烷基聚氧乙烯醚侧链发生解缔合,因而水溶液粘度迅速降低,SDS 分子对共聚物的分子链间疏水缔合作用影响不大,所以,其表观粘度变化不大.

REFERENCES

- 1 Mark H F, Bickales N M, Overberger C G. Encyclopedia of Polymer Science and Engineering, 2nd Ed. New York: Wiley, 1989. Vol 17: 730 ~ 735
- 2 Biggs S, Hill A, Selb J. J Phys Chem, 1992, 96: 1505 ~ 1511
- 3 Lunderg D J, Roberts S. J Appl Polym Sci, 1993, 49: 1509 ~ 1527
- 4 Stalol G A, Schulz D N. Water-Soluble Polymers for Petroleum Recovery. New York: Plenum Press, 1988. 6 ~ 10
- 5 Bock J, Donald B. U S Pat, C07f, 4528348. 1989-11-07
- 6 McCormic C L, Nandaka T, Jonhson C B. Polymer, 1988, 29: 731 ~ 739
- 7 Ezzel Sa, Hoyle C E, Greed D. Macromolecules, 1992, 25: 1887 ~ 1895
- 8 Hwang F S, Hagen-Esch T E. Macromolecules, 1995, 28: 3328 ~ 3335

STUDY ON SYNTHESIS AND PROPERTIES OF HYDROPHOBICALLY ASSOCIATING POLYACRYLAMIDE IN INVERSE MICROEMULSION

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Abstract Hydrophobically associating polyacrylamide (HAPAM) was prepared for the first time by inverse microemulsion polymerization. Its rheological properties were determined by using a Brookfield viscometer and compared with those of HAPAM prepared traditionally by micelle polymerization. Results showed that the apparent viscosity of the former kind of HAPAM increased with increasing co-polymer concentration and co-monomer content, even if when the co-polymer concentration was low. As for the latter kind of HAPAM, when the content of co-monomer increased to 1%, the apparent viscosity decreased so as to be lower than that of the copolymer of which the co-monomer content was 0.5%. In comparison, the former HAPAM won an advantage over the latter on salt resistance and shear stability. These results were interpreted in terms of hydrophobical associations in aqueous solutions which played an important role in rheological properties: in the macromolecular chain of the former HAPAM, hydrophobical co-monomers distributed randomly, but not in block. As a result, it was the intermolecular association instead of the intramolecular association predominated, which made the apparent viscosity increase remarkably and improved the salt resistance and shear stability.

Key words Hydrophobical association, Polyacrylamide, Inverse microemulsion, Apparent viscosity