

丙烯酰胺在聚乙二醇水溶液中聚合初期的液滴形成与成长过程^{*}

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摘 要 用动态激光光散射(DLS)在线观测了丙烯酰胺(AM)在聚乙二醇(PEG)水溶液中聚合初期液滴的出现、生长及聚并过程,考察了PEG分子量和浓度对聚合初期液滴尺寸的影响;用透射电镜(TEM)对聚合初期液滴形态的演变进行了观察,发现与DLS结果能很好吻合.用分光光度计对聚合体系分相点进行确定,采用溴化法测定了聚合体系临界分相时的转化率.随PEG分子量或浓度的升高,临界分相转化率逐渐减小;随温度的升高,临界分相转化率先减小后增大,在50℃左右出现最小值.用凝胶渗透色谱(GPC)对聚合体系临界分相时聚丙烯酰胺(PAM)的分子量进行了研究,变化趋势与临界分相转化率的变化一致.在上述基础上,提出了AM在PEG水溶液中聚合初期的液滴形成、成长机理.

关键词 丙烯酰胺, 双水相聚合, 临界分相转化率, 临界分子量

聚丙烯酰胺(PAM)是一种十分重要的水溶性高分子,广泛应用于污水处理、石油开采、造纸等行业.其制备方法主要是水溶液聚合,但仍存在聚合过程中的高黏度导致搅拌与传热等问题.反相(微)乳液聚合、在醇/水体系中的分散聚合,尽管克服了上述困难,并得到较高分子量的PAM,但引入的有机溶剂会造成污染,产品需要再分离.近年来,出现了水溶性单体的双水相聚合, Song等^[1,2]研究了丙烯酰胺(AM)在硫酸铵水溶液中的双水相聚合,单国荣等^[3~5]研究了AM在聚乙二醇(PEG)水溶液中的聚合动力学、产品稳定性.

双水相聚合反应是一种将水溶性单体、引发剂及分散介质溶解在水中,形成均相水溶液,一定条件下进行聚合反应,体系发生相分离,形成互不相容的水溶性聚合物分散液的聚合反应.关于传统分散聚合的成核机理,许多学者进行了深入研究^[6~12],认为随着引发剂的分解,聚合物自由基在连续相不断增长,达到临界链长时从连续相析出,并迅速聚并形成初级核,初级核不稳定,继续聚并直至被足够的稳定剂稳定,成核过程结束.成核过程时间很短,大约在转化率为0.1%时结束,之后不再形成新核,依靠聚合物粒子内部的聚合以及不断吸附连续相的聚合物自由基与链终止聚合物进行粒子的增长.目前,双水相聚合成滴机理的研究很少, Wang等^[13]研究AM/甲基丙烯酰氧

乙基三甲基氯化铵在硫酸铵水溶液聚合体系,认为反应一开始聚合物自由基与链终止聚合物聚集在一起形成聚合物相,随着界面张力的增强,小液滴在搅拌下逐渐形成.对双水相聚合初期液滴的形成、成长尚鲜有文献报道.

1 实验部分

1.1 实验原料

聚乙二醇(PEG, 分子量为4000、6000、10000、20000, 分别记为PEG4000、PEG6000、PEG10000、PEG20000)、丙烯酰胺, 均购于ACROS ORGANICS. 过硫酸铵(APS)、偶氮二异丙基咪唑啉盐酸盐(VA044)、硫代硫酸钠、碘化钾、溴酸钾、溴化钾、淀粉指示剂均为分析纯, 市售. 聚合用水为去离子水.

1.2 丙烯酰胺浓度及反应转化率的测定

按国标GB12005.3-89溴化法测定AM浓度, 计算聚合过程中AM的转化率.

1.3 聚合初期液滴尺寸和形态的表征

将一定量的PEG、AM与水混合, 溶解并降温后加入引发剂, 接着取其4 mL并用0.2 μm滤孔膜过滤后置于5 mL的比色皿中, 并在保护气体下密封. 然后将比色皿置于动态光散射(DLS)(Zetasizer 3000HSA, Malvern)检测槽中, 迅速升温至60℃, 开始计时, 在线检测聚合初期液滴的尺

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寸,每检测次耗时约 4 min.

取少量反应液分散在甲醇中,取少许滴于铜网上,干燥后用透射电镜(TEM)(JEOL JSM-1230EXT20)观察形态.

1.4 临界分相转化率及临界分子量的测定

称取一定量的 AM、PEG、去离子水,加到 500 mL 的夹套反应釜中,边搅拌(75 r/min)边通保护气体,升至指定温度,加入引发剂,开始计时.定时取样,用分光光度计(Shimadzu UV-3150)测其透光度.同时用溴化法测定转化率,将透光度开始下降时的转化率作为临界分相转化率.

待反应体系分相后加入终止剂对苯二酚停止反应,高速离心取其上层清液,去除水分,用甲醇洗涤数次去除 PEG.得到的产品干燥后用 GPC(Waters 1525 泵、2414 示差检测器、717 自动进样器)测定分子量,作为分相时的临界分子量.色谱柱由 PL aquagel-OH 50、30、10 型 3 柱串联.测试条件,流动相 0.1 mol/L NaNO_3 水溶液、流速 0.8 mL/min、试样浓度 0.3%、进样量 50 μL 、柱温 30 $^{\circ}\text{C}$.

2 结果与讨论

2.1 初期液滴尺寸与形态演变

采用 DLS 在线观测聚合反应初期 PAM 液滴的形成过程.反应开始后的前几次扫描中均未能检测到析出的 PAM 液滴,说明此时体系并未分相.随着反应的继续进行,DLS 检测到约为 30 ~ 50 nm 的微液滴,然后迅速增大,PAM 液滴滴径分布系数(DDI)先增大后减小,当转化率达到 6% 左右时,PAM 液滴滴径达到了约 200 nm.随着分散介质 PEG 分子量或浓度的减小,聚合物液滴稳定性下降,聚并加剧,液滴尺寸增大更加迅速,滴径分布系数变小,如图 1 和 2 所示.

采用透射电镜(TEM)对聚合初期的聚合物液滴形态进行了观察.由于在样品制备及 TEM 观察过程中会失水,不能确切地反映液滴的实际尺寸,但由于其液滴里富集了高含量的 PAM,其高黏度足够使其在样品制备或观察过程中维持原来的形态,因此液滴形态仍是准确的.如图 3(a)所示,在转化率较低时,其液滴形态为大小不均的球状;随后出现了椭球状形态的液滴(图 3b 所示),这是由于微液滴间发生聚并,但其液滴内部的高黏度阻碍了液滴间的扩散所致;随着反应的继续进行,从连续相析出聚合物液滴的速率增加,聚并

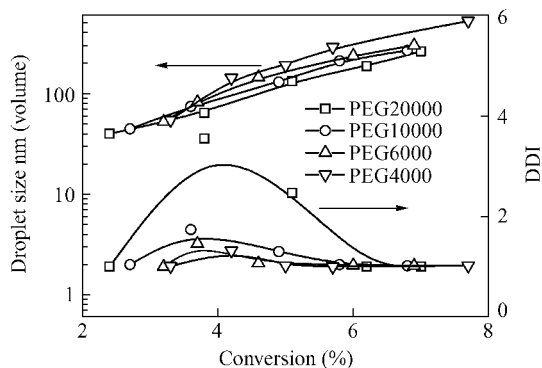


Fig. 1 Effect of PEG molecular weight on the droplets size and distribution in the initial stage of polymerization

PEG = 12 g, AM = 4 g, H_2O = 84 g, APS = 0.01 g, T = 60 $^{\circ}\text{C}$

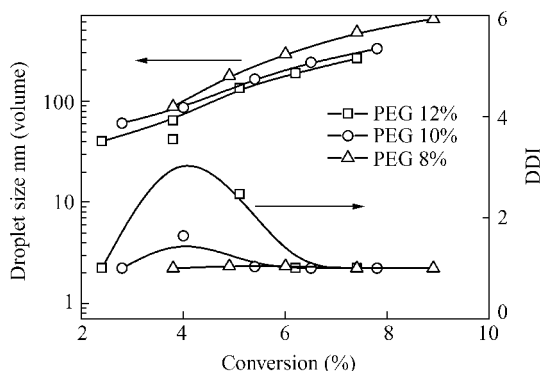


Fig. 2 Effect of PEG concentration on the droplets size and distribution in the initial stage of polymerization

PEG20000 + H_2O = 96 g, AM = 4 g, APS = 0.01 g, T = 60 $^{\circ}\text{C}$

加剧,较小液滴优先聚并,使得液滴尺寸变大,且较为均一(图 3c 所示).这些现象均与动态光散射结果相一致,但与 Wang 等^[13]研究所得结果有很大的差异.这是由于文献[13]是在硫酸铵水溶液体系中聚合,聚合初期的聚合物液滴含水率较高,内部黏度较低,且硫酸铵体系中液滴稳定性较差,其形态随着搅拌速率变化而改变.

2.2 临界分相转化率与临界分子量

为了进一步理解聚合初期液滴的形成机理,对 AM 在 PEG 水溶液中聚合分相时的临界分相转化率及临界分子量进行了测定.将反应液透光度下降时作为体系分相点,此时的转化率作为临界分相转化率(X_c). X_c 随 PEG 分子量(图 4)、PEG 浓度(图 5)的增加而下降,因此 DLS 能较早检测到微液滴(图 1、图 2 所示);随温度的上升(30 ~ 75 $^{\circ}\text{C}$)先减小后升高,50 $^{\circ}\text{C}$ 时的 X_c 达到了最小值(约为 1%)(图 6).这与 PEG-PAM- H_2O 双水相体系相图研究结果一致^[5].

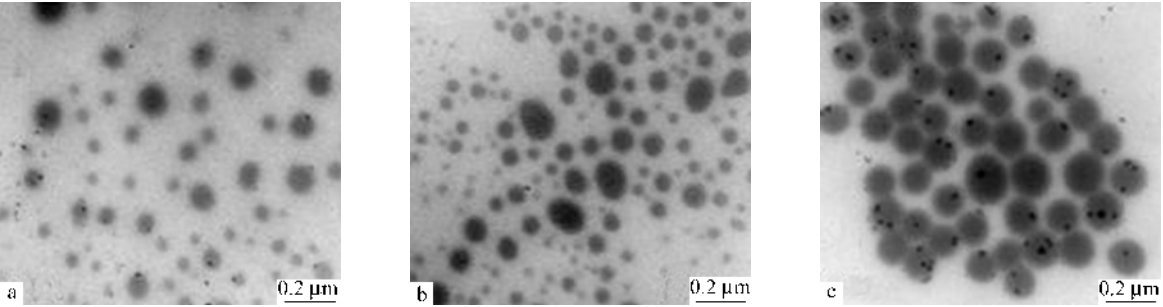


Fig. 3 Droplet morphologies in the initial stage
Conversion: a) 2.27% ; b) 3.43% ; c) 5.78% ; PEG20000 = 12 g, AM = 4 g, H₂O = 84 g, APS = 0.01 g, T = 60℃

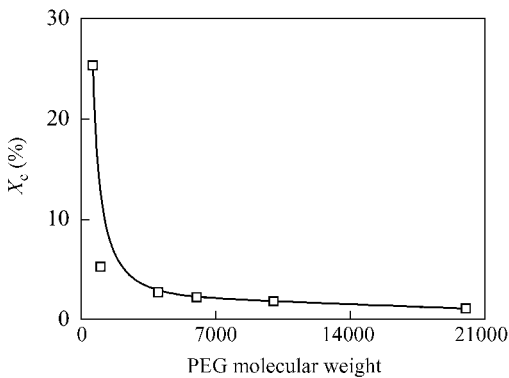


Fig. 4 Effect of PEG molecular weight on the critical conversion
PEG = 20 g, AM = 6 g, H₂O = 74 g, APS = 0.0025 g, T = 60℃

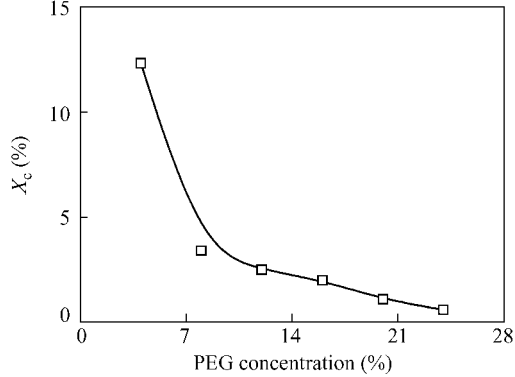


Fig. 5 Effect of PEG concentration on the critical conversion
PEG20000 + H₂O = 94 g, AM = 6 g, APS = 0.0025 g, T = 60℃

在 PEG 浓度为 20% 的反应体系中,当 PEG 分子量为 400 时,随着聚合反应的进行,体系始终清澈,未见相分离,最终产品 PAM 分子量较低(数均 58800、重均 433600)。这是由于 PEG 分子量下降,端羟基浓度增大,自由基向其链转移增多所致。而在 PEG20000 作为分散介质体系中,用量减少至 4% 时,转化率达到 12.5% 左右才发生分

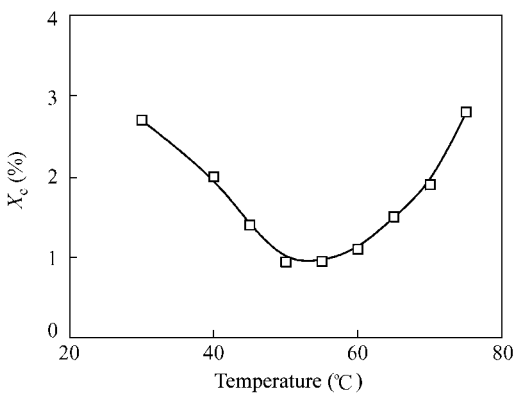


Fig. 6 Effect of polymerization temperature on the critical conversion
PEG20000 = 20 g, AM = 6 g, H₂O = 74 g, from 30℃ to 50℃ with VA044 = 0.0035 g, from 55℃ to 75℃ with APS = 0.0025 g

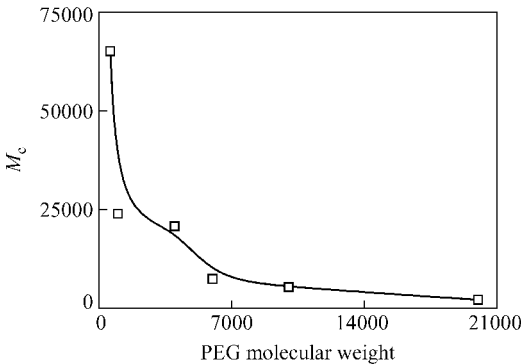


Fig. 7 Effect of PEG molecular weight on the critical molecular weight
PEG = 20 g, AM = 6 g, H₂O = 74 g, VA044 = 0.0035 g, T = 50℃

相,但体系不稳定,产品结块严重。

Yasuda 等^[12]曾对苯乙烯在乙醇中分散聚合的成粒机理进行了研究,并测定了其临界分子量,发现当搅拌转速为 30 r/min 时所测得的临界分子量最大,但随聚合温度及单体转化率的变化并

不显著. 图 7、图 8、图 9 是不同反应条件下 AM 在 PEG 水溶液中聚合临界分相时的 PAM 临界分子量(M_c),其变化趋势与 X_c 相一致. 随聚合温度上升, M_c 先减小后增大,在 50℃ 时,出现了最小值,约为 2227. 随 PEG 浓度或分子量的减小, M_c 逐渐增大,从连续相析出的 PAM 链聚并形成的初始微液滴尺寸也随之增大(图 1、图 2 所示).

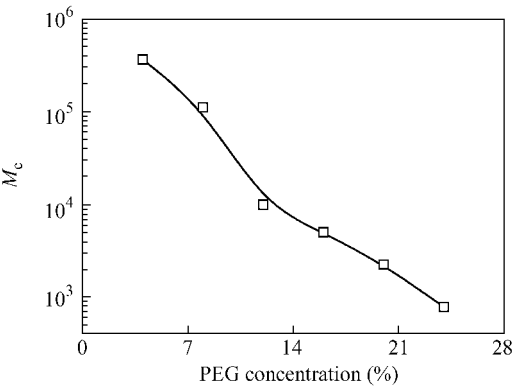


Fig. 8 Effect of PEG concentration on the critical molecular weight
PEG20000 + H₂O = 94 g, AM = 6 g, VA044 = 0.0035 g, T = 50℃

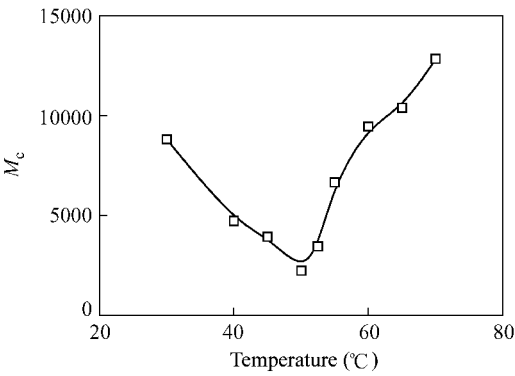


Fig. 9 Effect of polymerization temperature on the critical molecular weight
PEG20000 = 20 g, AM = 6 g, H₂O = 74 g, from 30℃ to 50℃ with VA044 = 0.0035 g, from 55℃ to 75℃ with APS = 0.0025 g

2.3 聚合初期液滴形成、成长机理

反应开始后,由于引发剂分解,聚合物自由基不断生成并增长,见图 10 中的 I 和 II. 当聚合物自由基达到临界链长时,从连续相中析出,并迅速聚并,形成初级核,见图 10 中的 III. 初级核不稳定,继续聚并,形成微液滴,见图 10 中的 IV,到此为止,将其定义为液滴形成期.

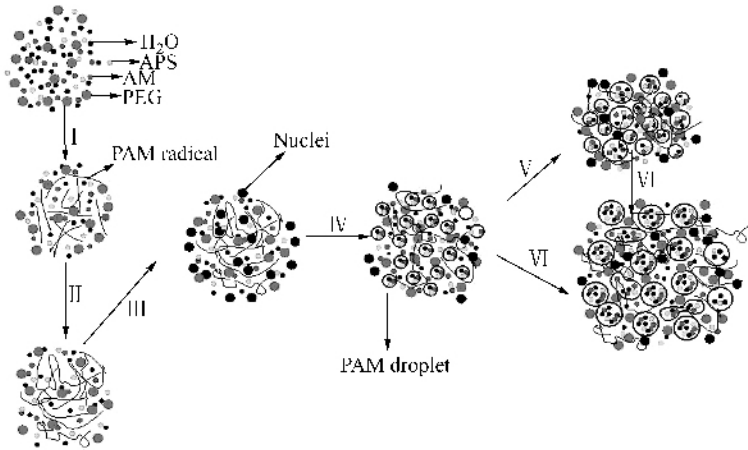


Fig. 10 Schematic representation of the initial droplets formation and growth mechanism of AM aqueous two-phase polymerization in aqueous PEG solution

聚合反应在连续相及聚合物相同时进行,微液滴通过内部聚合不断长大;同时连续相又不断析出形成新的微液滴,液滴滴径分布开始变宽,见图 10 中的 V. 随反应进行,液滴数目不断增多,尺寸较小的液滴优先聚并,使得聚合物液滴滴径增大且分布重新变窄,见图 10 中的 VI. 实验中发现,由于聚合初期液滴间的聚并较为激烈,当聚合速

率过快时,在聚合初期即形成细凝胶状 PAM,产品静置后极易分层. 因此要制备较为稳定的乳状分散液产品,控制初期的聚合速率十分关键.

3 结论

AM 在 PEG 水溶液中聚合开始后,由于引发剂分解,聚合物自由基不断生成并增长,当聚合物

自由基达到临界链长时,开始从连续相中析出. X_c 与 M_c 随 PEG 分子量或浓度的增加而减少,随着温度的上升先减小后增大,在 50℃ 时达到了最小值. 随后析出的聚合物链迅速聚并形成初级核,初级核不稳定,继续聚并形成微液滴,这个阶段定义为液滴形成期. 此后,聚合反应在连续相及聚合物

相同时进行,微液滴通过内部聚合不断长大,同时又从连续相析出新生成的微液滴,因此其液滴滴径分布开始变宽. 随着反应的继续进行,液滴数目不断增多,尺寸较小的液滴优先聚并,使得液滴尺寸增大,并变得较为均一.

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INITIAL DROPLETS FORMATION AND GROWTH PROCESS OF
ACRYLAMIDE DURING AQUEOUS TWO-PHASE POLYMERIZATION IN
AQUEOUS POLY(ETHYLENE GLYCOL) SOLUTION

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Abstract In order to explore the droplet formation process of the aqueous two-phase polymerization of acrylamide (AM) in aqueous poly(ethylene glycol) (PEG) solution, dynamic light scattering (DLS) was employed to investigate the appearance, the size and size distribution of droplets in the initial stage of polymerization. The effects of PEG molecular weight and concentration on the droplets size and distribution were studied. It was found that the droplets stability in aqueous PEG solution decreased, and the droplets aggregated with each other to form larger and more uniform droplets with decreasing PEG molecular weight or PEG concentration. The morphology of the droplets rich in polyacrylamide (PAM) was observed with transmission electron microscopy (TEM). The droplets shape in the initial stage of polymerization is spherical but polydisperse. However, some oval droplets formed in the product, while the conversion was still very low, which indicated some coalescence of droplets in this stage. As the polymerization proceeds, the droplet size increased rapidly and the size distribution of droplets become uniform. These results were well in agreement with the DLS results. With using the spectrophotometer, the phase separation point was determined where the

transparence of reaction solution declined suddenly. The effect of various parameters on the critical conversion of phase separation was measured by bromating method. It decreased with the increase of PEG molecular weight or PEG concentration. With raising temperature from 30℃ to 70℃, the critical conversion decreased at first, and then turned to increase when the temperature was at about 50℃. The critical molecular weight was also systemically investigated by gel permeation chromatogram (GPC). It could be seen that the evolution of critical molecular weight corresponded well with that of critical conversion at various reaction conditions. On the basis of above mentioned results, an initial droplet formation and growth mechanism of AM aqueous two-phase polymerization in aqueous PEG solutions was proposed. As the reaction starts, primary radicals, generated by decomposition of the initiator, grow in the continuous phase by the addition of monomer units until they reach their critical chain length. Then these polymer radicals precipitate and aggregate to form nuclei. The nuclei are not stable, and they will immediately aggregate with each other to form tiny droplets. Then monomer and initiator diffuse into the droplets rapidly, and polymerization takes place in both the continuous phase and the dispersed phase (inside the droplets). In the earlier stage, the PAM droplets are stable and grow mainly by polymerization inside the droplet. Because new smaller droplets generate from continuous phase at the same time, the droplet size distribution becomes wide. However, these droplets become unstable with the polymerization and aggregate with each other to make the droplet size distribution become narrow again.

Keywords Acrylamide, Aqueous two-phase polymerization, Critical conversion, Critical molecular weight