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Atom Transfer Radical Polymerisation in Emulsion

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SUMMARY: Atom transfer radical polymerisation ATRP) has been applied to emulsion systems using 2-pyridinecarbaldehyde-3,3-diphenylpropylimine (dPP) and 4,4'-diheptyl-2,2'-bipyridine (dHbpy) as ligands in the Cu-complex. The application of the former shows a jump in molecular weight at low conversion, probably due to the slow build-up of deactivating species in the particle phase. When dHbpy is used as ligand, control over polymerisation is maintained up to higher conversion, which is due to the favourable partitioning of the deactivator. The absence of initial high molecular weight can be ascribed to the faster build-up of the deactivator concentration in the particle phase. The preliminary results show that ATRP in emulsion is possible, but additional investigations are necessary to understand the role of all components involved.

Introduction

Free-radical polymerisation is the most widely used technique to produce commercially applied polymers. It has important advantages when compared to living techniques such as ionic polymerisation, since it is applicable to a variety of monomers and more robust regarding impurities. A major disadvantage, however, is the occurrence of transfer and termination reactions, which limit the fine-tuning of polymer properties such as end-group functionality, molecular weight distribution and, in the case of copolymers, chemical composition distribution.

Recently, several techniques have been developed that allow control over the polymerisation, while maintaining the benefits of free-radical polymerisation[1,2,3,4)]. The most promising and versatile of them seems to be Atom Transfer Radical Polymerisation (ATRP)[3,4)]. In this system, the growing polymer radicals ($P_n\cdot$) are reversibly 'trapped' by a halide atom (X), usually a bromine or chlorine. A transition metal complex, usually a copper complex, in its reduced state (M^n) is able to accept the halide upon which it is oxidised to M^{n+1}. The general mechanism of ATRP is depicted in scheme 1:

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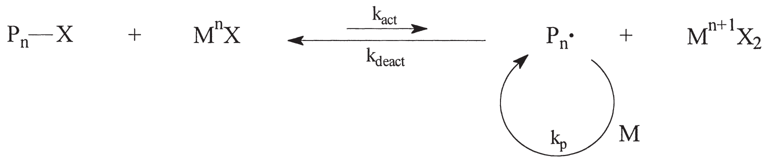
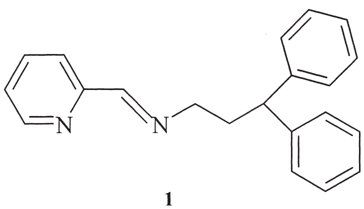


Scheme 1. General mechanism of ATRP.

ATRP enables the relatively easy production of e.g. block[5)] and gradient[6,7)] copolymers and application of ATRP in emulsion systems would therefore offer great industrial possibilities. Some attempts to perform controlled polymerisation in emulsion have been reported[8,9,10,11)]. In this paper we will discuss the ATRP homopolymerisation of methyl methacrylate (MMA) and the integration of it in emulsion systems.

Various components

Metal complex. The most important component in ATRP is without any doubt the transition metal complex that acts as the catalyst. In this work, copper is used as the transition metal. The copper complex should not only have a suitable redox potential in order to perform well in ATRP, but in emulsion also an optimal partitioning between the water phase and organic phase. The choice of ligands is, therefore, of paramount importance. Two classes of ligands that work very well in homogeneous ATRP are the Schiff-base ligands[12)] and the substituted bipyridines[13)]. In order to obtain sufficient partitioning of the catalyst, we have synthesised 2-pyridinecarbaldehyde-3,3-diphenylpropylimine (**1**, dPP) and 4,4'-diheptyl-2,2'-bipyridine (dHbpy). A qualitative assessment of the partitioning of the Cu(I)/dPP complex was carried out, and it was concluded that sufficient water solubility was attained to allow transport of the complex through the aqueous phase to the micelles and polymer particles in an emulsion polymerisation. The largest fraction of the complex was present in the organic phase (based on visual inspection of the intensity of the colour of the two phases)



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Surfactant. Since interaction with the catalyst should be avoided at all times, non-ionic surfactants are the best choice as emulsifiers for ATRP in emulsion. In our research, we have made use of polyoxyethylene alkyl phenyl ethers, which all have a cloud point above 100°C and are effective in high electrolyte concentrations.

Initiator. In ATRP, alkyl halides that resemble the monomer structure are mostly used as the initiator. For instance, in the ATRP of methyl methacrylate (MMA) ethyl-(2-bromo)-isobutyrate is used. In traditional emulsion polymerisation, initiation takes place in the water phase and, after entry of the oligomer, propagation takes place in the particle. We can use the same mechanism in ATRP in emulsion by using 2-hydroxyethyl-2'-bromopropionate. Since this compound has one stabilising methyl group less compared to its isobutyrate analogue, initiation will be slower and, in addition, bimolecular self-termination forming dimers will be more pronounced.

Water. Figure 1 shows the effect of water on the ATRP of MMA in bulk with a copper/dPP complex. It is clear that the addition of water enhances the polymerisation rate. The reason for the rate increase is not known, although the activating effect of water while retaining control over the polymerisation has been previously reported by Granel *et al.*$^{14)}$ for polymerising MMA with rhodium and palladium. A parallel can be drawn with the increase of reaction rate by the addition of phenols, which has been reported by Haddleton *et al.*$^{15)}$.

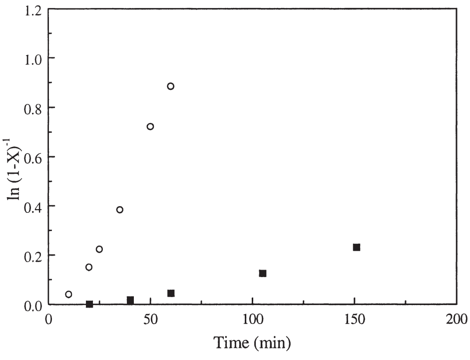

Figure 1. The effect of the addition of water to a bulk ATRP of MMA at 90°C with a copper/dPP complex (▪ without water, ○ saturated with water). MMA/CuBr/Et-2-BriB=125/1/1

Emulsion ATRP with dPP

Emulsion ATRP experiments have been carried out with methyl methacrylate (MMA) in various concentrations and at temperatures ranging from 60°C to 85°C. Antarox CO-880 was used as surfactant, since it showed good stabilising ability. Furthermore, CuBr was used with dPP as the complexing ligand.

The kinetic plot and the evolution of the number average molecular weight (M_n) versus conversion (X) of a typical emulsion ATRP experiment are depicted in figure 2 and 3, respectively.

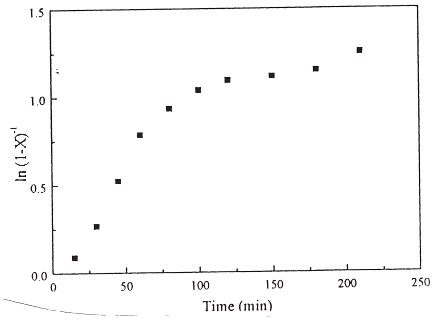

Figure 2. $\ln(1-X)^{-1}$ vs. time for an emulsion ATRP of MMA at 80°C with dPP. MMA/CuBr/Initiator=500/1/1.6

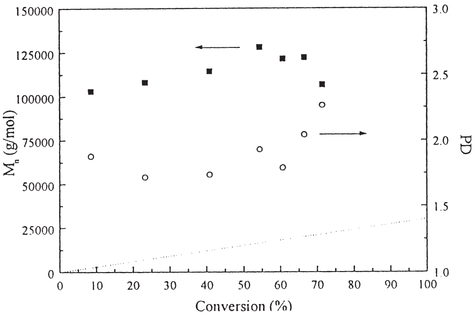

Figure 3. M_n vs. conversion for an emulsion ATRP of MMA at 80°C with dPP. Dashed line is the theoretical curve for M_n. Conditions as in figure 2.

It is uncommon to use the $\ln(1-X)^{-1}$ vs. time plot in case of emulsion polymerisation, since the monomer concentration is expected to remain constant in interval II (and not decay exponentially as in bulk or solution polymerisation). However, since the emulsion polymerisation of MMA at low monomer concentration is known to enter interval III at a conversion as low as 30%, the major part of the polymerisation should lead to a linear behaviour in the plot. This obviously only holds under the assumption that the number of particles in the emulsion polymerisation is constant.

When we take a closer look at the experiments with dPP, three important features catch the eye. First of all, from figure 2 it can be seen that the reaction rate is dropping at about 65% conversion. The apparent rate coefficient, k_p^{app}, which is the slope of the $\ln(1-X)^{-1}$ vs. time plot, can be expressed as follows (in interval III):

$$k_p^{app} = k_p \cdot [P_n\cdot] = k_p \cdot \frac{k_{act}}{k_{deact}} \cdot \frac{[P_nX][Cu^I]}{[Cu^{II}]} \tag{1}$$

A decreasing k_p^{app} therefore means that either the equilibrium shifts towards the dormant species, or the concentration of this species is decreasing, or that the ratio of $[Cu^I]/[Cu^{II}]$ is decreasing.

A second important observation is the high molecular-weight polymer that is formed at low conversion (figure 3). This molecular weight jump at low conversion indicates that polymerisation must have taken place according to the classical free radical mechanism. The oligomeric radical in the water phase is assumed to enter the particle as an active species that behaves like a free radical, probably in the absence of a Cu^{II} complex. This hypothesis is supported by the fact that lowering the CuBr concentration leads to an increase of the initial molecular weight jump, regardless of temperature and initiator concentration.

A third peculiarity is the decrease of M_n after 60% conversion and, together with this, an increase of the polydispersity. Since M_n is dropping, the reason for this should be transfer to monomer. Furthermore, the resulting small chains thus formed are highly mobile and are likely to give more termination. This would also explain the decreasing reaction rate after 65% conversion.

Emulsion ATRP with dHbpy

To investigate the influence of the ligand, experiments were also carried out with dHbpy as complexing agent. The results are displayed in figure 4 and 5.

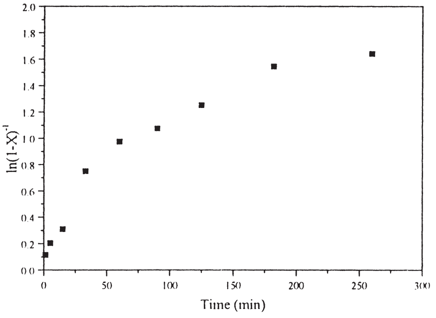

Figure 4. $\ln(1\text{-}X)^{-1}$ vs. time for an emulsion ATRP of MMA at 70°C with dHbpy. MMA/CuBr/Initiator=400/1.5/1

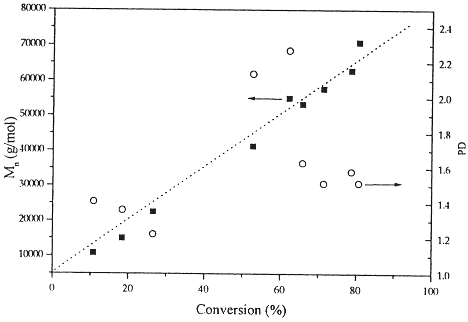

Figure 5. M_n vs. conversion for an emulsion ATRP of MMA at 70°C with dHbpy. Dashed line is the theoretical curve for M_n. Conditions as in figure 4.

From figure 5 it is clear that M_n follows the theoretical line almost perfectly. Polydispersities, apart from two samples, stayed relatively low during the whole coarse of reaction. However, when taking a look at the $\ln(1\text{-}X)^{-1}$ vs. time plot, a decrease in reaction rate can still be noticed. This decrease in reaction rate can be explained when taking a closer look at the molecular weight distributions for all samples (figure 6):

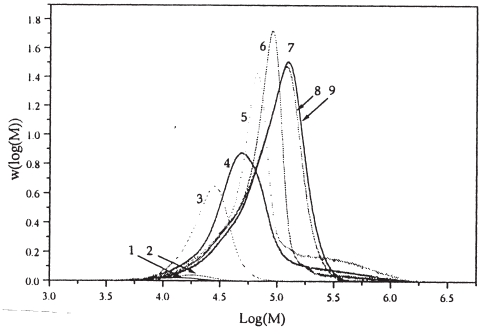

Figure 6. Molecular weight distributions for an emulsion ATRP with dHbpy.

From figure 6, it is clear that molecular weights increase with conversion and that we are dealing with a controlled polymerisation. However, at a certain point, i.e. sample number 6, a low-molecular weight tail appears that results from dead polymer. This dead material must have been formed by termination reactions and not by transfer, since the number average molecular weight is behaving according to theory. The number of growing chains is therefore decreasing, while the total number of chain remains constant. This hypothesis is further supported by the observed decreasing reaction rate. Note that the high molecular-weight material in chromatograms 4 and 5 is responsible for the high polydispersity in figure 5 and is probably due to an SEC artefact.

These preliminary experiments result in latices with broad particle size distributions as measured by transmission electron microscopy. No attempts have been undertaken so far to obtain narrow distributions. The colloidal stability of the latices was satisfactory, although a minor amount of sedimentation was observed after several days. During the polymerisation, there was no scale formation on the reactor wall and stirrer.

Conclusions

ATRP in emulsion is possible when using dPP/copper and dHbpy/copper complexes. The former shows control up to 65% conversion, after which control over polymerisation is lost. Furthermore, a jump in molecular weight is observed at low conversion, which is due to the slow build-up of deactivator in the particle phase. The dHbpy/copper complexes show good control during the entire reaction, although some termination takes place. Probably, the partitioning of the copper complex, especially the complex in its oxidised state, is more favourable when using dHbpy as ligand. The absence of an initial molecular weight jump can be explained by the faster build-up of deactivating species in this case. The preliminary results indicate that ATRP in emulsion is very promising, but additional investigations concerning partitioning of the copper complex and reaction mechanism are necessary.

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