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Polymer 41 (2000) 1697–1702

polymer

N-alkyl-2-pyridinemethanimine mediated atom transfer radical polymerisation of styrene: the transition from heterogeneous to homogeneous catalysis ☆

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Received 16 December 1998; received in revised form 8 April 1999; accepted 12 April 1999

Abstract

The polymerisation of styrene was studied using $Cu^{(I)}/Cu^{(II)}$-based atom transfer radical polymerisation catalysts in conjunction with a variety of *N*-alkyl-2-pyridinemethanimines as complex ligands. Increasing the length of alkyl chain on the ligand from propyl to octyl resulted in a catalyst complex with improved solubility in xylene, and enabled the production of polymers of narrower molecular weight distribution. The molecular weight distribution was further narrowed by changing the solvent to a more polar system, diglyme, in which case polymers with $(M_w/M_n) = 1.1–1.2$ were produced, and the catalyst system generated shows possibility of being amenable to kinetic study. The narrow molecular weight distribution is consistent with a soluble catalyst promoting rapid exchange of a halogenated chain end into an active form. Crown copyright © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerisation; Styrene; Polymerisation

1. Introduction

Atom transfer radical polymerisation (ATRP) appears to be one of the most universal and widely applicable of the numerous examples of controlled radical polymerisation techniques reported, allowing the controlled polymerisation of styrenic [1–3], methacrylic [4–7,9] and acrylic [8] monomers of a variety of architectures. ATRP is believed to proceed via the establishment of a fast equilibrium between dormant halogen end-capped polymer chains and active propagating radicals (Scheme 1), with the process typically being catalysed by a transition metal complex capable of existing in more than one oxidation state.

A variety of transition metal complexes have been utilised for this role, but $Cu^{(I)}$ halides complexed by α-diimine ligands seem to be extremely effective and the most widely studied. Three distinct classes of α-diimine ligand have been reported: 2,2′-bipyridines [1–4,8], 1,10-phenanthrolines [10] and *N*-alkyl-2-pyridinemethanimines [5,9,11–13]. Of these, *N*-alkyl-2-pyridinemethanimines appear to be the most interesting, as they are known to be more effective at stabilising metals in low oxidation states than either of the other alternatives [14]. Therefore, the use of *N*-alkyl-2-pyridinemethanimine derivatives in ATRP should result in an enhanced deactivation step, compared to bipyridyl and phenanthroline, imparting the potential to afford a higher degree of control over polymerisation. To this effect, we have been investigating their use in the ATRP of styrene. This communication reports some preliminary results of our investigations.

2. Experimental

2.1. Materials

Styrene (Aldrich) was distilled from sodium hydroxide onto calcium hydride, where it was stored until required. Xylene (Fisher) was stored over calcium hydride until required. CuBr (Aldrich), 1-phenyl ethyl bromide (Lancaster) and diglyme (Aldrich) were used without further purification. *N*-Propyl-2-pyridinemethanimine (PPMI) and *N*-octyl-2-pyridinemethanimine (OPMI) were synthesised by condensation of the appropriate alkyl amine with 2-pyridinecarboxaldehyde using standard literature procedures [5].

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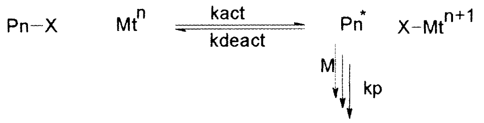
PII: S0032-3861(99)00283-9



Scheme 1.

2.2. Polymerisation

All polymerisations were conducted by heating a solution of styrene/CuBr/ligand/1-phenyl ethyl bromide (1-PEBr) in the ratio of 100:1:3:1, using xylene as solvent so that the volume ratio of styrene:xylene was 1:1. The required amounts of styrene and xylene were distilled under high vacuum directly into a polymerisation vessel containing CuBr and ligand. The solution was then subjected to three freeze-pump-thaw degassing cycles after which 1-PEBr was added. In the case of polymerisations utilising diglyme instead of xylene, the solvent was added subsequent to the freeze-thaw degassing process. The solution was heated to 100°C under argon and polymerisation of the monomer took place; samples were withdrawn at intervals. Polymerisations involving PPMI as ligands were conducted as single batch experiments, as the heterogeneity of the reaction media meant that the withdrawal of representative samples from a polymerisation was impossible.

2.3. Characterisation

In all cases monomer conversion was determined by gravimetry. Molecular weights and molecular weight distributions were determined using a Polymer Labs gel permeation chromatograph fitted with guard, Plgel 10^3 A°, Plgel mixed B columns with THF as eluent at 40°C.

3. Results and discussion

As a result of the reported tolerance of the ATRP process to a number of functional groups, we are interested in its application to the polymerisation of functionalised derivatives of styrene. Hence, prior to the utilisation of this class of catalysts for the polymerisation of more sophisticated monomers, we decided to investigate the behaviour of ATRP in the polymerisation of styrene itself. Given the reports in the literature, concerning the effect of structure of the complexing ligand on the efficiency of catalysis, we investigated first the effect of the structural differences on the polymerisation of styrene in a series of *N*-alkyl-2-pyridinemethanimine derivatives. This effect is shown in Fig. 1, with the use of OPMI leading to the formation of polymers with the most narrow molecular weight distributions (1.2) and molecular weights close to the theoretical values; i.e. number average molecular weights calculated from 100% efficiency of the initiator. It was observed that PPMI gave a system that was heterogeneous whereas the OPMI ligand formed a completely homogeneous catalyst. However, it should be noted that increasing the solubility of the catalyst complex changes the profile of the polymerisation rate. Fig. 2 shows the conversion-time curves for the series of catalyst systems under study and indicates that the soluble system generates a slower rate of polymerisation than the PPMI heterogeneous system. It seems probable that this is associated with an increase in the concentration of

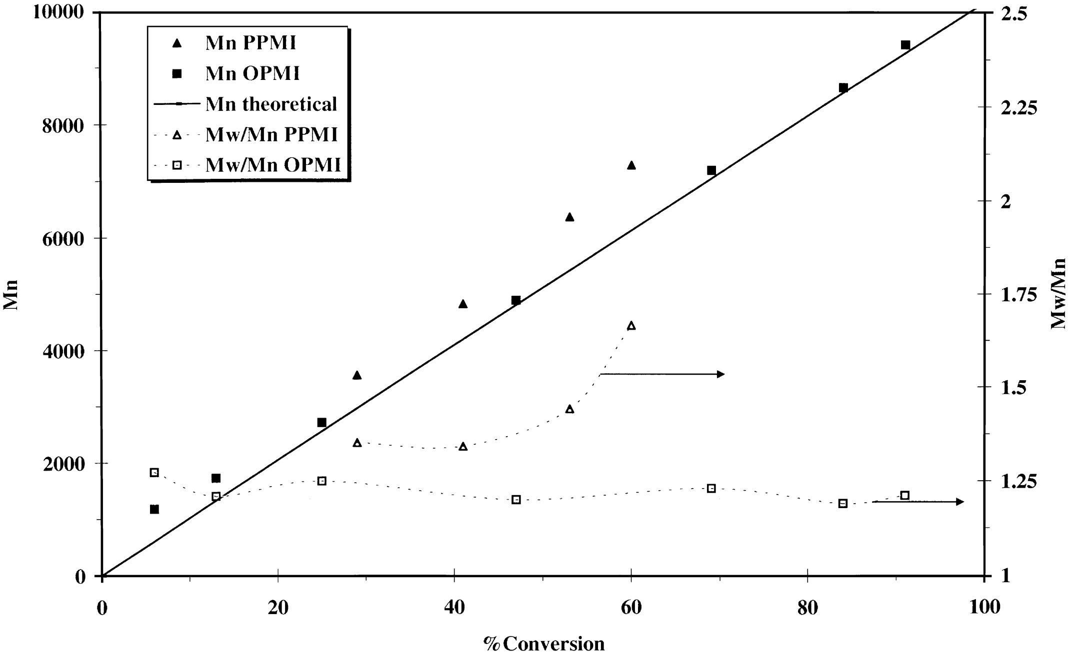


Fig. 1. Dependence of number average molecular weight and polydispersity on conversion. Closed symbols indicate molecular weight values, open symbols represent polydispersity values.

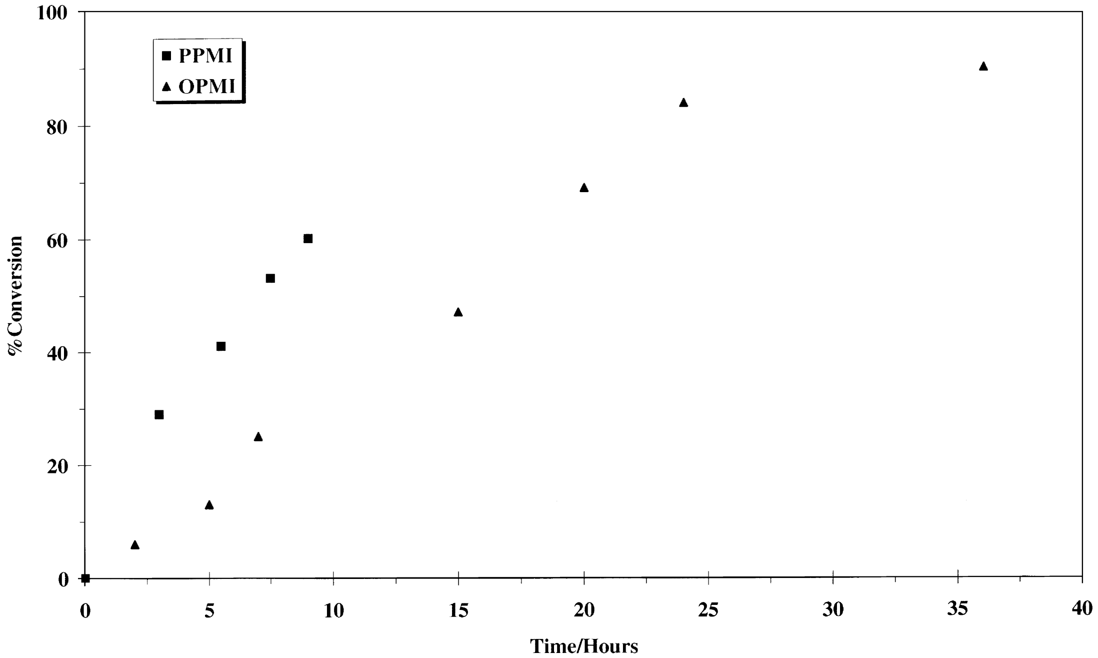


Fig. 2. Dependence of conversion on time for the polymerisation of styrene mediated by $Cu^{(I)}$/2-pyridinemethanimine complex.

catalyst-forming centres, which in turn generates a more efficient atom transfer deactivation step. However, we feel that such soluble catalyst systems are much more amenable to kinetic study than the heterogeneous systems such as those using PPMI as ligand. Similar observations for the 2,2′-bipyridyl system have been made by Matyjasewski [2] and Percec [15].

The narrowing of the molecular weight distribution associated with the more soluble catalyst system might at first sight be incompatible with the slow build-up to the maximum rate of polymerisation, which is explained by a slow increase in the concentration of catalyst sites. However, we should consider the halogenated end-group of the initiator or propagating chain to be only a precursor of the active centre. Also, the concentration of the active centres is determined not only by the concentration of

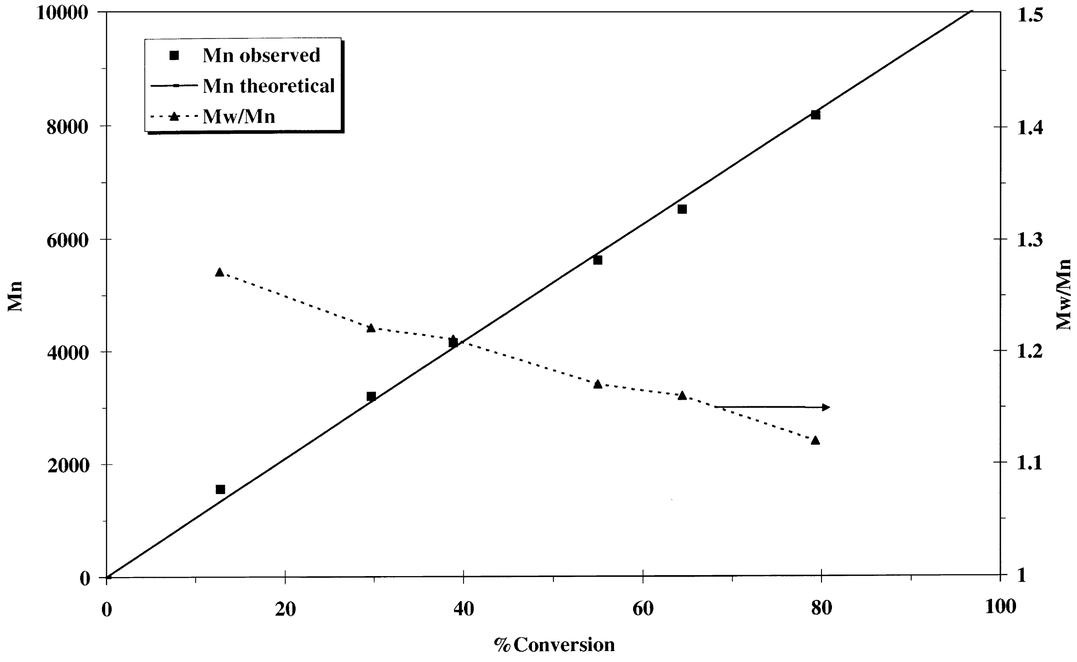


Fig. 3. Dependence of number average molecular weight and polydispersity on conversion for ATRP of styrene conducted in diglyme.

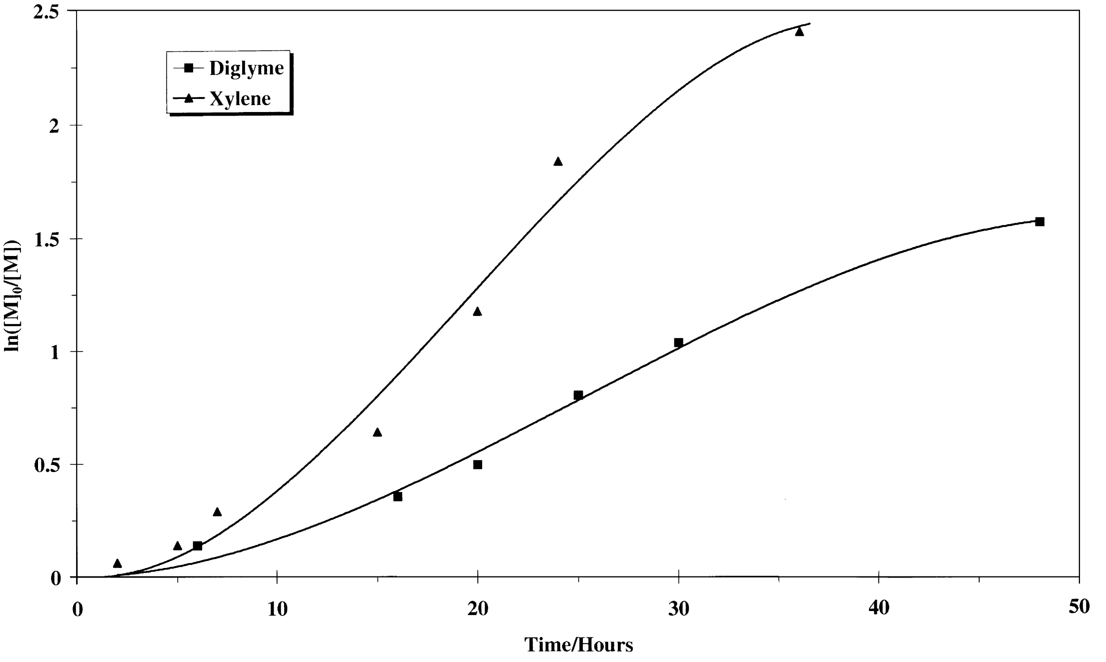


Fig. 4. Pseudo-first order kinetic plots for ATRP of styrene conducted in xylene and diglyme.

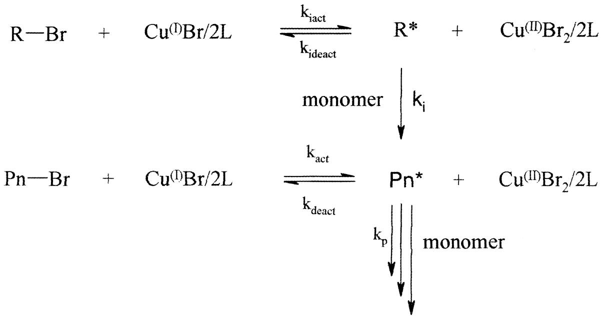
polymer chains, but also by the concentration of copper species present in the correct form or same oxidation state. Effectively, the end group of the polymer chain acts as a reservoir of active centres, and the molecular weight distribution will be narrow as long as they are transformed in a rapid equilibrium reaction. If this be the case, then statistically it is likely that the halogenated chain ends will spend identical proportions of time in the propagating and dormant states, irrespective of the concentration of $Cu^{(II)}Br_2$/ligand deactivating species.

If the polydispersity of the polymer is used as a measure of the efficiency of initiation, it would appear from the data on the use of OPMI as a ligand that the attainment of a soluble catalyst system is desirable. In an attempt to develop an efficient catalyst system, we investigated the effect of a more polar solvent, diglyme, on the polymerisation of styrene using OPMI as the ligand in the conventional ATRP catalyst system. It is evident from the data shown in Fig. 3 that the molecular weight distributions of the products of these polymerisations are considerably narrower than those obtained from a heterogeneous system. Moreover, a very close correlation exists between the experimentally determined and theoretical values of number average molecular weight for the polymers. Again, it is of importance to note that the maximum rate of polymerisation decreased when the catalyst complex used is soluble in the reaction medium and the pseudo-first order plot is non-linear (Fig. 4).

The lower rate of polymerisation observed for polymerisations conducted in diglyme solution may be due to enhanced solubility and a higher active concentration of the deactivating $Cu^{(II)}Br_2$/ligand species, which in turn would lead to a more efficient deactivation process and a lower steady state concentration of propagating species.

This lowering of the polymerisation rate may also be rationalised by considering diglyme as a species, which has the ability to co-ordinate with and deactivate the catalyst. Haddleton reported that the addition of phenol or methyl hydroquinone [12,13,16] to the ATRP of methyl methacrylate (MMA), conducted in xylene solution, results in an increase in the rate of polymerisation. Here, the role of the phenol is defined as co-ordinating with the Cu centre and displacing a diimine ligand to form the active catalytic species. Matyjasewski has also reported that the active catalytic species in the ATRP of MMA appears to be a one to one ligand to $Cu^{(I)}Br$ complex [17], with such species having a vacant co-ordination site which in some way facilitates propagation. However, contrary to this it has been reported [2] that the active catalytic species in the ATRP of styrene appears to be a two to one ligand to $Cu^{(I)}Br$ complex. Indeed if this be the case, then the co-ordination of diglyme with the Cu centre and the consequent displacement of a ligand will result in the deactivation of the active catalyst, and thus a decrease in the rate of polymerisation.

Alternatively, the lower rate of polymerisation observed in diglyme may simply be due to solvation effects, whereby the enhanced solubility of the catalyst complex in diglyme solution confers the existence of a greater solvation shell around the catalyst complex than that apparent in xylene solution. Such a phenomenon would hinder interaction between the active catalyst complex and the halogen end-capped chain, effectively decreasing the concentration of propagating species and hence decreasing the rate of polymerisation.



Scheme 2. Cu(I)/(II)/ligand complexes are denoted as $Cu^{(I)}Br/2L$ and $Cu^{(II)}Br_2/2L$, respectively.

The curvature of the kinetic plots (Fig. 4) is notable and is in each case indicative of a gradual increase in the concentration of propagating species during the early stages of the reaction, until a "steady-state" is achieved, after which the concentration of propagating species and rate of polymerisation decreases.

Considering the mechanism of $Cu^{(I)}Br/\alpha$-diimine mediated ATRP (Scheme 2), the curvature of the plots in the initial stages may be due to a relatively slow initiation process, but may also be indicative of the formation of a steady-state concentration of active $Cu^{(II)}Br_2/2L$ and propagating species. This is consistent with the observations of Matyjasewski [18] and Fukuda [19], who illustrated that the concentration of the deactivating $Cu^{(II)}Br_2/2L$ complex gradually increases over a period of one hour until a steady state concentration, approximately 5% of the total Cu concentration is present as $Cu^{(II)}Br_2/2L$ with the remainder present as $Cu^{(I)}Br/2L$, is established via the persistent radical effect [20].

Our observations illustrate this process clearly, allowing the following profile to be envisaged. The reaction of $Cu^{(I)}Br/2L$ with the initiator results in the formation of active initiating and propagating species and $Cu^{(II)}Br_2/2L$, with the concentration of each of the former species increasing with time. Due to the relatively low concentration of $Cu^{(II)}Br_2/2L$ in the early stages of polymerisation, the rate of deactivation is found to be slow. Hence, the time the chain-ends spend in the active form is relatively large, facilitating bimolecular termination reactions and irreversible formation of an excess of $Cu^{(II)}Br_2/2L$. As this process continues, the concentration of $Cu^{(II)}Br_2/2L$ species gradually increases and therefore the efficiency of the deactivation process increases, decreasing the rate of termination and thus increasing the concentration of chains participating effectively in a dynamic ATRP equilibrium. Subsequently, after a given period of time, the concentration of $Cu^{(II)}Br_2/2L$ is found to be sufficiently large such that it sustains an efficient deactivation process, suppressing the termination and maintaining a maximum concentration of active centres, and therefore allowing the polymerisation to proceed in a controlled manner under steady state conditions with a maximum rate of polymerisation. The apparent deviation from this steady state at high conversion probably coincides with a decrease in the concentration of potentially active chain-ends via termination reactions. It is of importance to note that this increase in the occurrence of termination reactions does not result in broadening of the molecular weight distribution, and it is therefore apparent that such termination steps result simply in the loss of chain-end functionality. However, it is also probable that the decrease in the rate of polymerisation is manifested as a result of monomer consumption or the conversion of the catalyst to inactive states.

4. Conclusion

In summary, we have demonstrated that the solubility of the $Cu^{(I)/(II)}$/*N*-propyl-2-pyridinemethanimine complex can be increased by increasing both the length of the pendant alkyl chain and the polarity of the solvent. Increasing the solubility increases the inherent degree of control afforded over the polymerisation, but decreases the rate of polymerisation. The sigmoidal nature of the kinetic plots illustrates the role of the "persistent radical effect" in the establishment of steady-state conditions. This phenomenon is currently under further investigation in our laboratory.

Acknowledgements

Financial support for the work by the Defence Evaluation Research Agency is recognised. C. Wyres also acknowledges the Engineering and Physical Sciences Research Council (CASE award) for financial support.

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