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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 30 June 2001

To cite this Article Beers, Kathryn L. and Matyjaszewski, Krzysztof(2001) 'THE ATOM TRANSFER RADICAL POLYMERIZATION OF LAURYL ACRYLATE', *Journal of Macromolecular Science, Part A*, 38: 7, 731 – 739

To link to this Article: DOI: 10.1081/MA-100103876

URL: <http://dx.doi.org/10.1081/MA-100103876>

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NOTE

THE ATOM TRANSFER RADICAL POLYMERIZATION OF LAURYL ACRYLATE

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ABSTRACT

The atom transfer radical polymerization (ATRP) of dodecyl (or lauryl) acrylate (LA) has been studied and optimized to yield polymers with predetermined molecular weights and low polydispersities. The poor solubility of the catalyst complex formed with linear tridentate amines and Cu(I)Br in both LA and the non-polar solvents required for the formed poly(lauryl acrylate) (pLA) resulted in poor control of the polymer molecular weights and high polydispersity. The use of a soluble catalyst formed by complexing copper with 4,4'-di(5-nonyl)-2,2'-bipyridine, improved both molecular weight control and polydispersities. The experimental conditions were further optimized by adding deactivating Cu(II) complex to the initial reaction mixture to compensate qualitatively for differences in the rate of termination relative to other acrylates.

Key Words: Controlled/living radical polymerization; Atom transfer radical polymerization; ATRP; Ligands; Lauryl acrylate.

A great deal of literature has been published in recent years regarding the application of atom transfer radical polymerization (ATRP) to a variety of monomers under various conditions [1, 2]. Starting with the classical system of polymerization of styrene in bulk and working up to functional monomers in polar

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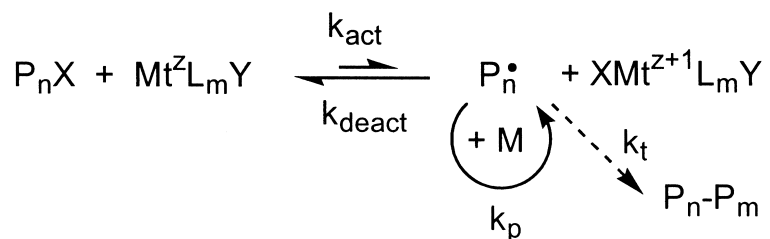
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solvents, each time a monomer has been added to the library of those polymerizable by ATRP, the conditions change slightly [3-22]. These changes were generally intended to accommodate changes in the reactivity of the propagating chain, the strength of the carbon-halogen bond of the dormant chain and the solubility of the monomer, polymer and catalyst. Similarly, when the architecture of the polymer becomes more complex, the conditions that may have yielded well-defined linear polymers, often cannot be applied. For example, multi-armed stars [23-25], densely grafted chains [26] and polymacromonomers [27] were prepared by ATRP under radically different reaction conditions than their linear analogues.

Hence, when we undertook the controlled polymerization of a highly hydrophobic, non-polar, fairly bulky monomer, such as dodecyl or lauryl acrylate (LA) by ATRP (Scheme 1), there were fundamental changes in the rate of termination and solubility, which mandated changing the reaction conditions from those typically used for other acrylates. This note along with previous reports suggest that a basic understanding of the reaction mechanism along with prudent choices of solvents, initiators and catalyst are needed for each monomer [14, 15, 17], and often for more complex architectures.

In the activation step, with the rate constant k_{act} , a metal complex $\text{Mt}^z\text{L}_m\text{Y}$ cleaves the carbon-halogen bond of P_nX reversibly and homolytically, generating a carbon-centered radical species P_n^\bullet . Radical adds to the monomer with the rate constant k_p , before it is deactivated, with the rate constant k_{deact} , by the metal complex $\text{XMt}^{z+1}\text{L}_m\text{Y}$ to form the dormant species P_nX . Through these reversible and repetitive cycles, well-defined polymers with high molecular weight are formed. Since the concentration of radicals is very low, termination, k_t , often can be neglected.

A more precise description about how the catalyst controls the polymerization through the atom transfer equilibrium is given in Equations 1 and 2. $[\text{I}]_0$ refers to the initial concentration of the initiator. In Equation 1, the rate of polymerization, R_p , is first order with respect to the monomer, $[\text{M}]$, and the Cu(I) concentration in solution. A high concentration of Cu(II) slows down the rate of polymerization. Not only does the rate constant of propagation, k_p , which is specific for each monomer, affect R_p , but also the rate constants for activation, k_{act} , and deactivation, k_{deact} . Equation 2 provides means for understanding how the molecular



Scheme 1.

weight distribution, M_w/M_n , decreases with conversion, p . A narrower molecular weight distribution is obtained at higher conversion, higher k_{deact} relative to k_p , higher concentration of deactivator and higher molecular weights, i.e., $1/[I]_0$. At the limit of fast propagation and slow deactivation, ATRP simply becomes a conventional redox-initiated radical polymerization process resulting in a high polydispersity polymer. Fast deactivation requires sufficiently high concentration of Cu(II), which can be either added in advance or formed via persistent radical effect [28].

$$R_p = k_p \cdot \frac{k_{\text{act}}}{k_{\text{deact}}} \cdot [M][I]_0 \cdot \frac{[Cu^I]}{[XCu^{II}]} \quad (1)$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p [I]_0}{k_{\text{deact}} [XCu^{II}]} \right) \cdot \left(\frac{2}{p} - 1 \right) \quad (2)$$

We have recently reported that CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) and tris(2-(dimethylamino)ethyl)amine (TREN) are both efficient and inexpensive multidentate ligands for Cu-based ATRP of several acrylates [29-31]. The optimized conditions for the ATRP of *t*-butyl and *n*-butyl acrylate have been established previously [19] and include the use of the PMDETA/Cu(I)Br complex and the addition of a cosolvent such as acetone or anisole to solubilize the deactivating Cu(II) species. The ATRP of LA under these conditions lead to an initially homogeneous solution from which both the Cu(II) species and eventually poly(lauryl acrylate) (pLA) precipitated with increasing conversion. The polarity of the polymer and the catalyst is different enough that solvents for the catalyst are poor solvents for the polymer and vice versa. As the Cu(II) precipitated out of solution, the rate of reversible deactivation decreased and the amount of irreversible termination increased, generating more Cu(II). The observable results were both the precipitates and higher polydispersities (Figures 1 and 2) [32, 33]. Molecular weights increased linearly with conversion but they remained below the theoretical values; the consistent discrepancy was attributed to a difference in hydrodynamic volume between pLA and the polystyrene standards, used to calibrate the GPC.

When the complexing ligand was switched to 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy), there was increased compatibility between the long, lipophilic alkyl chains on the ligand and the monomer. Upon heating, the solution of catalyst in monomer became homogeneous and no precipitation was observed during the polymerization. This eliminated the need for a cosolvent (only an internal standard of 5 v/v% toluene was used). The polydispersity, although decreased with conversion, remained high throughout the reaction (Figure 2). The GPC traces (Figure 3) clearly show a second peak of higher molecular weight, which dimin-

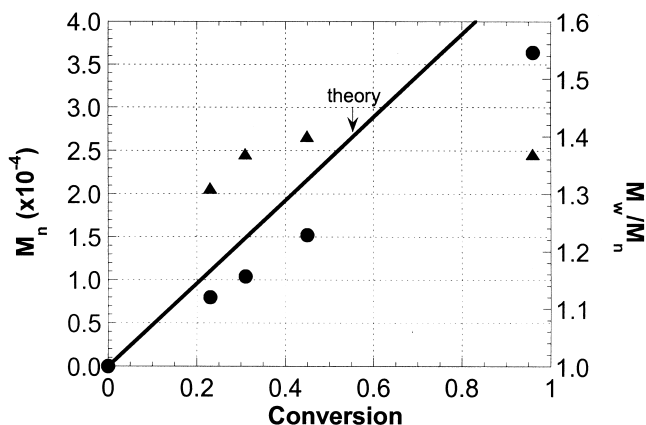


Figure 1. Molecular weight versus conversion plot for the ATRP of lauryl acrylate. [LA] = 2.9 M in acetone, [MPB] = 14.7 mM, [CuBr(PMDETA)] = 7.4 mM, T = 60°C (● - M_n , ▲ - M_w/M_n).

ished in intensity as the conversion increased. Additionally, the low molecular weight edge of the principal peaks are broadened by tailing, which is most prominent in the low conversion samples. This indicates that there was a large amount of conventional polymerization and irreversible termination by both coupling and disproportionation, at the beginning of the reaction. Likewise, disappearance of the peak into the baseline at longer reaction times indicated that eventually more Cu(II) species formed, such that reversible deactivation could compete with termination. The fact that dead chains were still being formed continuously is evident in the continued low molecular weight tailing.

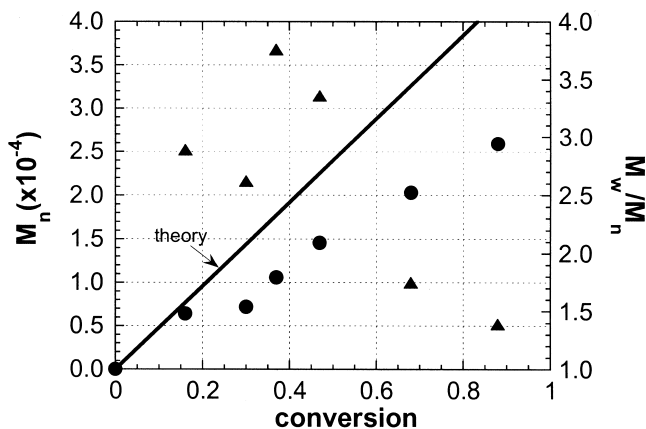


Figure 2. Molecular weight versus conversion plot for the ATRP of lauryl acrylate. [LA] = 3.5 M in toluene, [MPB] = 17.3 mM, [CuBr(dNbpy)₂] = 17.3 mM, T = 90°C (● - M_n , ▲ - M_w/M_n).

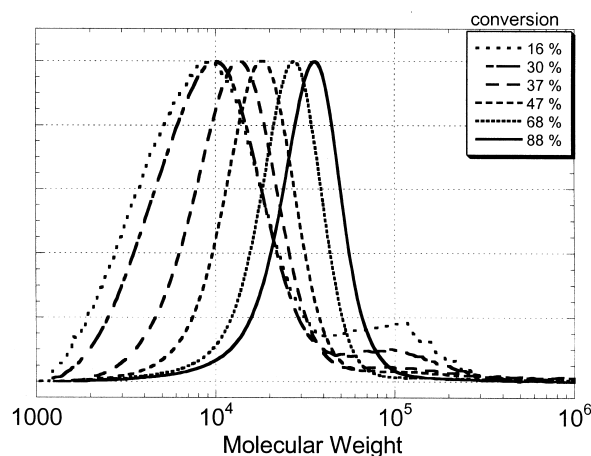


Figure 3. GPC traces at various conversions for pLA prepared by ATRP. [LA] = 3.5 M in toluene, [MPB] = 17.3 mM, [CuBr(dNbpy)₂] = 17.3 mM, T = 90°C.

The competition between conventional and controlled radical polymerization is more clearly observed in the ATRP of LA than in other acrylic monomers such as methyl acrylate (MA) under comparable conditions. The key difference between the two monomers is the rate constant of termination, k_t . Recent pulsed laser polymerization measurements have shown that $k_t(\text{MA}) > 16k_t(\text{LA})$, whereas the rate constants of propagation, k_p , of the two monomers are approximately the same, with k_p of LA being 50% higher than that of MA [34]. This may be explained by a steric effect, in which the dodecyl group effectively screens the free radical chain end from bimolecular termination reactions. Termination reactions at the beginning of the ATRP are responsible for the generation of the deactivator, Cu(II), necessary to provide sufficiently fast deactivation to reduce the radical concentration and mediate propagation [28]. Without establishing a sufficient concentration of Cu(II), the concentration of radicals is too high resulting in uncontrolled polymerization. This scenario is accentuated in the ATRP of LA relative to the homopolymerization of macromonomers, in which the k_t is strongly suppressed, but propagation is also slower [35].

When the ATRP of LA using the dNbpy/CuBr catalyst was repeated with 4 mol% CuBr₂ added relative to CuBr at the beginning of the reaction, the high molecular weight shoulder and low molecular weight tailing was no longer present. Polydispersities were lower (Figure 4) and GPC traces became symmetric and monomodal (Figure 5).

The rates of polymerization are plotted in Figure 6.

The long alkyl side group in LA substantially changed the polymerization environment for ATRP. The less expensive and more efficient catalyst, CuBr(PMDETA) is not effective in this case, because of the poor miscibility of

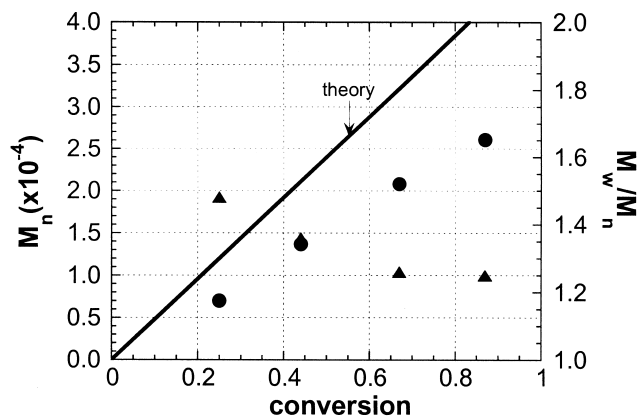


Figure 4. Molecular weight versus conversion plot for the ATRP of lauryl acrylate. [LA] = 3.5 M in toluene, [MPB] = 17.3 mM, [CuBr(dNbpy)₂] = 17.3 mM, [CuBr₂] = 0.7 mM, T = 90°C (● - M_n , ▲ - M_w/M_n).

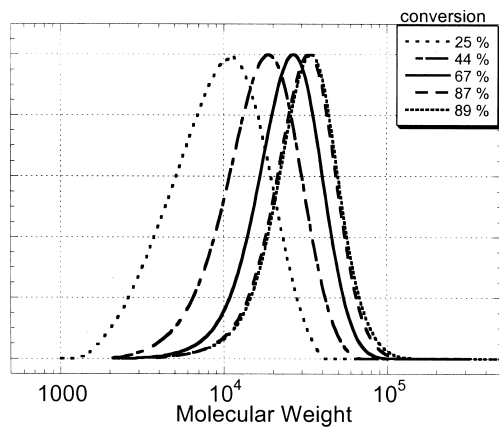


Figure 5. GPC traces for pLA prepared by ATRP. [LA] = 3.5 M in toluene, [MPB] = 17.3 mM, [CuBr(dNbpy)₂] = 17.3 mM, [CuBr₂] = 0.7 mM, T = 90°C.

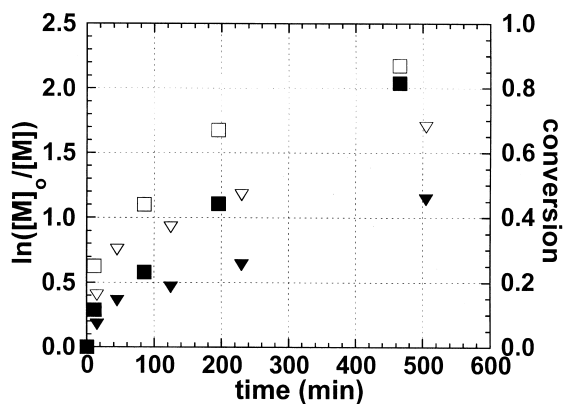


Figure 6. First order kinetic plot for the ATRP of lauryl acrylate. [LA] = 3.5 M in toluene, [MPB] = 17.3 mM, [CuBr(dNbpy)₂] = 17.3 mM, T = 90°C. For ▽ - conversion and ▼ - $\ln([M]_0/[M])$, [CuBr₂] = 0 mM. For □ - conversion, ■ - $\ln([M]_0/[M])$, [CuBr₂] = 0.7 mM.

the polymer, pLA, in solvents for the deactivating Cu(II) species. Using the more expensive alkyl substituted bipyridine ligands instead of PMDETA yields a homogeneous catalyst solution without requiring a cosolvent. A low rate of termination in LA polymerization lead to high molecular weight polymer at low conversions if additional deactivating species (Cu(II)) was not present in the solution. The polymerization was controlled, however, if Cu(II) was added at the beginning of the reaction.

ACKNOWLEDGMENTS

We would like to thank the industrial sponsors of the ATRP Consortium at CMU for their financial support. We are also grateful to Dr. Kelly Davis for helpful discussions.

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32. CuBr was washed with acetic acid followed by methanol to remove impurities. CuBr₂ was ground with a mortar and pestle to improve the rate of dissolution. 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy) was prepared as described elsewhere. LA was dissolved in hexanes, washed with 5% sodium hydroxide and dried over magnesium sulfate. The hexanes were removed under vacuum and the monomer was passed through alumina to remove polymerization inhibitors. All other reagents were used as received.
Example procedure for the ATRP of LA: LA (2.5 mL; 9.2 mmol) and dNbpy (0.0755 g; 0.18 mmol) were dissolved in 2.5 mL toluene and nitrogen gas was bubbled through the solution while stirring for 45 minutes. CuBr (0.0129 g; 0.09 mmol) was added and an initial kinetic sample was taken by syringe. The solution was bubbled with nitrogen for an additional 10 minutes until homogeneous and the flask was placed in a 90°C oil bath. Methyl 2-bromopropionate (MBP; 10 mL) was added and samples were removed at timed intervals. After 6.75 hours, the conversion was 59 % (1H NMR). $M_{n,th} = 14,200$, $M_n, GPC = 12,400$, $M_w/M_n = 1.26$.
33. Gas chromatography was performed on a Shimadzu GC14-A. NMR spectra were recorded on a Bruker WM300 in deuterated chloroform. A Waters 510 LC Pump connected to a Waters 410 differential refractometer with THF as the carrier solvent and linear, 500, 1000Å and guard Phenogel columns were used for gel permeation chromatography (GPC). Molecular weights were measured versus polystyrene standards.
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Received January 30, 2001