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Preparation of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization. 3. Effect of Reaction Conditions on the Self-Condensing Vinyl Polymerization of 2-((2-Bromopropionyl)oxy)ethyl Acrylate

Krzysztof Matyjaszewski* and Scott G. Gaynor

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue,
Pittsburgh, Pennsylvania 15213

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ABSTRACT: The homopolymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate (BPEA) by atom transfer radical polymerization (ATRP), a "living"/controlled radical polymerization system, has yielded a hyperbranched polymer. Variation of the reaction conditions and especially the concentration of copper(II) in the polymerization system affects not only the rate of polymerization but also the chain architecture. The copper(II) concentration in the polymerization medium is affected by solvent, the ligand used to complex copper, and temperature. The effects of temperature and ligand on the polymerization rate and the resulting chain architecture were studied.

Introduction

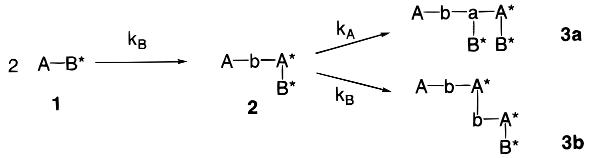
The synthesis of dendritic polymers has received much attention in the past few years.[1,2] The reason is that these dense, highly branched polymers are expected to have different physical properties than their linear analogs. The major impediment to their commercial development has been that these polymers generally require multiple step syntheses, with purification of the dendrimer/dendrons at each step.

Hyperbranched polymers have been developed as an alternative to dendrimers, as they can be prepared in a single, one pot reaction. Originally proposed by Flory,[3] the first hyperbranched polymers were prepared by Kim and Webster[4,5] by the cross-coupling of AB_2 functionalized phenyl rings. Since this development, a wide variety of hyperbranched polymers have been prepared from AB_2 monomers by condensation polymerizations.[6−11]

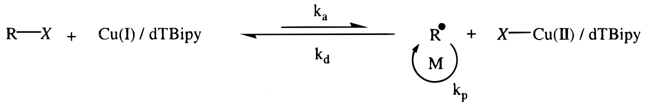
Recently, the synthesis of hyperbranched polymers has been extended to functionalized vinyl monomers[12−18] by a method termed self-condensing vinyl polymerization, SCVP.[12] The functionalized vinyl monomers have been described as AB* monomers where the double bond is denoted A and the functional group is B*.[19] The B* group is capable of being activated to form a propagating center which can initiate the polymerization of the double bond (A) on the monomer, Scheme 1. After addition of one or more monomer units and deactivation of the propagating species, two sites, A* or B*, can now be activated to reinitiate the polymerization. Ideally, the reactivity of all the groups, A*, B* or double bond, are the same in monomer and polymer, as in a conventional step growth process.

The relative reactivities of the two active sites, $r = k_A/k_B$, has a profound effect on the architecture of the final polymer. If either k_A or k_B is strongly favored over the other, then predominately linear polymers will be obtained. For $k_A \sim k_B$, a branched polymer is expected. For polymerization systems in which an equilibrium is established between active and dormant species and the reactivities of A* and B* are intrinsically the same, the value r can be correlated with the number of monomer units added to an active site before being deactivated.[20]

Scheme 1



Scheme 2



The value of $r = k_A/k_B$ can be estimated from the proportion of B* in the molecule and can be used to determine the degree of branching (DB) (DB = 0 for a linear polymer and DB = 1 for a perfect dendrimer).[20] It was calculated that when $r = 1$, DB = 0.465; the DB reached a maximum DB = 0.5, when $r = 2.6$.[21]

The polymerization system that we have used is atom transfer radical polymerization, ATRP.[22−24] This is a "living"/controlled radical polymerization which establishes a dynamic equilibrium between active radicals and dormant species by the use of a redox reaction between lower oxidation transition metal salts, e.g., copper(I), and alkyl halides, Scheme 2. This equilibrium must lie predominately to the left ($K << 1$, $K = k_a/k_d$, the ratio of the rate constansts of activation and deactivation) so as to have only a small concentration of radicals present in the polymerization system and to have most polymer chain ends dormant (R−X = initial alkyl halide, P−X = polymer with a halide end group(s)). However, if the equilibrium lies too far to the left, the polymerization becomes very slow or does not occur. On the other hand, if the equilibrium is too far to the right, an uncontrolled polymerization is obtained, similar to peroxide/iron(II) redox initiation systems.

The polymerization of vinyl monomers by ATRP has allowed for the synthesis of well-defined polymers ($DP_n = \Delta[M]/[I]_o$, $M_w/M_n < 1.5$). It has also displayed a wide versatility in the range of monomers and initiators that can be used. The monomers include styrenes,[22−24] acrylates,[22] methacrylates,[22,25−29] and acrylonitrile.[30,31] The only requirement for an initiator is that it must contain an activated halogen group; the halogen must

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be adjacent to a group which can stabilize the resulting radical, e.g., benzyl halides, α-haloketones (esters), $R-SO_2$, and α-halonitriles. The polymerization of vinyl monomers by ATRP has been shown to obey the rate law defined in eq 1; the polymerization is first order in monomer, initiator, and copper(I), while the rate is inversely proportional to copper(II).[24] This equation will be fundamental in subsequent discussions about the polymerization of hyperbranched polymers by ATRP.

$$R = k_p[M][R^\bullet] = k_pK[M][R-X]\frac{[Cu(I)]}{[Cu(II)]} \qquad (1)$$

It has been demonstrated that well-defined polymers ($M_w/M_n < 1.5$) could be obtained with heterogeneous catalyst systems (ligand = 2,2′-bipyridyl(Bipy)),[22] but even better control ($M_w/M_n < 1.1$) of the polymerization was obtained when homogeneous catalyst systems (ligand = 4,4′-di-(5-nonyl-2,2′-bipyridine (dNBipy)) were used.[23,24,32,33] This increase in the control of the polymerization has been attributed to an increase in the concentration of copper(II) relative to copper(I),[23] which allows for a faster rate of deactivation of the propagating radical. When the ratio of the rate of propagation to deactivation (R_p/R_d) is lowered, fewer monomer units are added to an active center before being deactivated, resulting in the preparation of well-defined, linear polymers.[34]

Initially, when polymerizing acrylic AB* monomers by ATRP, we used a copper(I)/4,4′-di-*tert*-butyl-2,2′-bipyridine (dTBipy) catalyst system to polymerize 2-((2-bromopropionyl)oxy)ethyl acrylate, BPEA.[17,18] In an effort to improve the materials, i.e., to increase the degree of branching, completely homogeneous catalyst systems were used (dNBipy). However, this did not enhance the polymerization rate; in contrast, the polymerization did not occur. This paper describes how the reaction conditions played a pivotal role in determining the copper(II) concentration and its subsequent effect on the rate of polymerization and the final architecture of the polymer prepared from the same monomer, BPEA.

Experimental Section

General Data. All chemicals were from Aldrich Chemical Co., Inc. The monomer, 2-((2-bromopropionyl)oxy)ethyl acrylate, BPEA, was prepared according to the previously reported procedure.[17,18] *p*-(Chloromethyl)styrene, CMS, (98% para isomer) was purified by passing through alumina to remove inhibitor, followed by distillation under reduced pressure. 4,4′-Di-tert-butyl-2,2′-bipyridine (dTBipy) and 4,4′-di-5-nonyl-2,2′-bipyridine (dNBipy) were prepared by coupling of the respective pyridines in the presence of 5% Pd−C (10 w/v %, Pd−C to pyridine) after heating to 150 °C (dTBipy) or 200 °C (dNBipy) for 1 week.[24] 2,2′-Bipyridyl (Bipy) was used as received. Copper(I) halides were purified by stirring in glacial acetic acid, washing with ethanol, then drying under vacuum at 70 °C.

UV spectra were obtained on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer in 1 cm quartz cells. Copper(II) solutions were prepared in sealed flasks by dissolving the copper(II)/ligand in the respective solvent and stirring overnight. Extinction coefficients, ϵ, were determined from Beer's law by successive dilution of a solution of the copper species in the respective solvent. Oxygen sensitive solutions of copper(I) were prepared under nitrogen and measured using a 1 cm quartz cell with a glass joint; the cell was attached to a Schlenk flask.

^{1}H NMR were obtained in $CDCl_3$ using a 300 MHz Brüker NMR with TecMAG processing software. Molecular weights were obtained by size exclusion chromatography (SEC) using a Waters 510 pump, a Waters WISP 712 autosampler, and a Waters 410 differential refractometer with 5μ Waters Styrogel columns (guard, 0.5HR, 4E HR, 5HR). The data were processed using Polymer Standards Service software with linear polystyrene standards.

Polymerizations. To a dry, 10 mL, round-bottom flask, with a magnetic stir bar, ligand (2 equiv for dTBipy or dNBipy, 3 equiv for Bipy) and CuI Br (1 equivalent) were added. The flask was sealed with a rubber septum and the contents of the flask placed under vacuum, and the flask was then backfilled with nitrogen (3×) to remove oxygen. Degassed BPEA (100 equiv) was added, and the reaction mixture was then stirred at the desired temperature. Samples were taken periodically to monitor the conversion of the double bonds (^{1}H NMR) and the molecular weight growth with conversion (SEC). All NMR and SEC results were obtained from unprecipitated samples; i.e., they contain unreacted monomer. Analysis of ^{1}H NMR spectra were performed as previously described.[20]

Saturated Copper(II) Solutions. The desired concentration of the $Cu^{II}X_2$ solutions was 1.0 M. The solutions were stirred at room temperature to prevent polymerization/decomposition of the monomer. To a 5 mL flask with a magnetic stir bar were added $Cu^{II}X_2$ (X = Cl (CMS); X = Br (BPEA)) and ligand (2 equiv for dTBipy or dNBipy; 3 equiv for Bipy), and the flask was sealed with a rubber septum. Monomer was added via syringe and the mixture stirred for 18 h at room temperature. The solutions were then filtered through a PTFE 0.45 μm filter and analyzed by UV/vis. The solutions were diluted as necessary to achieve an absorbance of less than 2.

Results and Discussion

Originally, the homopolymerization of BPEA by ATRP was conducted at 100 °C using copper(I) bromide/dTBipy, as the catalyst.[18] The ligand, dTBipy, did not yield completely homogeneous copper(I) solutions, and when the reaction was performed at 50 °C, after 6 h it provided a polymer with $M_n = 2050$, $M_w/M_n = 6.9$ (based on linear polystyrene standards) in >99% yield with the percentage of B* groups corresponding to a degree of branching DB = 0.49. In an attempt to improve the structural features of the prepared polymer, a homogeneous catalyst was used, copper(I) bromide/dNBipy. However, when the polymerization was carried out at 100 °C, using the more soluble catalyst, no polymer was obtained even after five days, Figure 1. Polymer was only obtained at higher temperatures, i.e., 130 °C, when this highly soluble catalyst was used. Unfortunately, a side reaction was observed, which will be discussed later.

When the less soluble catalyst, copper(I) bromide/Bipy was used, polymer was obtained at 100, 80, and 50 °C. In contrast to the use of dNBipy as the ligand, the rate of polymerization was fast when the polymerization was conducted at either 80 or 100 °C; the reaction had reached completion before 30 min at these temperatures, Figure 1. Only at 50 °C was the polymerization slow enough to conveniently monitor the rate of polymerization.

Evaluation of the molecular weights of the final polymers obtained in the polymerizations using Bipy showed that M_n decreased with increasing temperature, Figure 2. The reaction at 50 °C using dTBipy is shown as a reference.

The high molecular weights obtained were attributed to slow deactivation of the propagating radical. To enhance the rate of deactivation, two experiments were performed to increase the concentration of copper(II) in the solution. These were to add a small amount of copper(II) bromide or dNBipy (0.1 equiv relative to Cu(I)Br or 0.1 mol % relative to monomer) to the

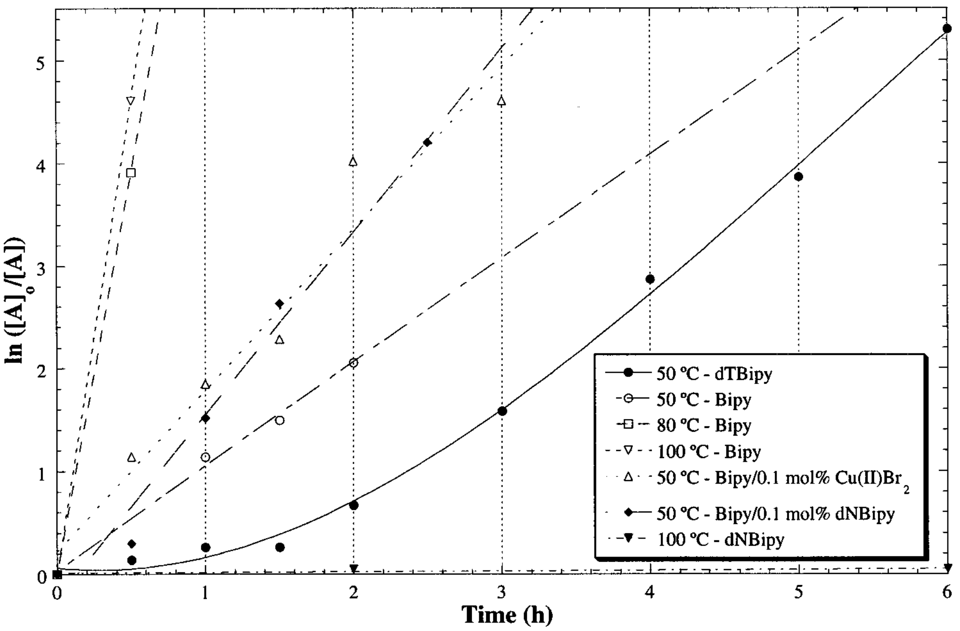


Figure 1. First-order kinetic plots for the homopolymerization of BPEA by ATRP under various reaction conditions. For all, Cu^I Br was 1 mol % relative to monomer.

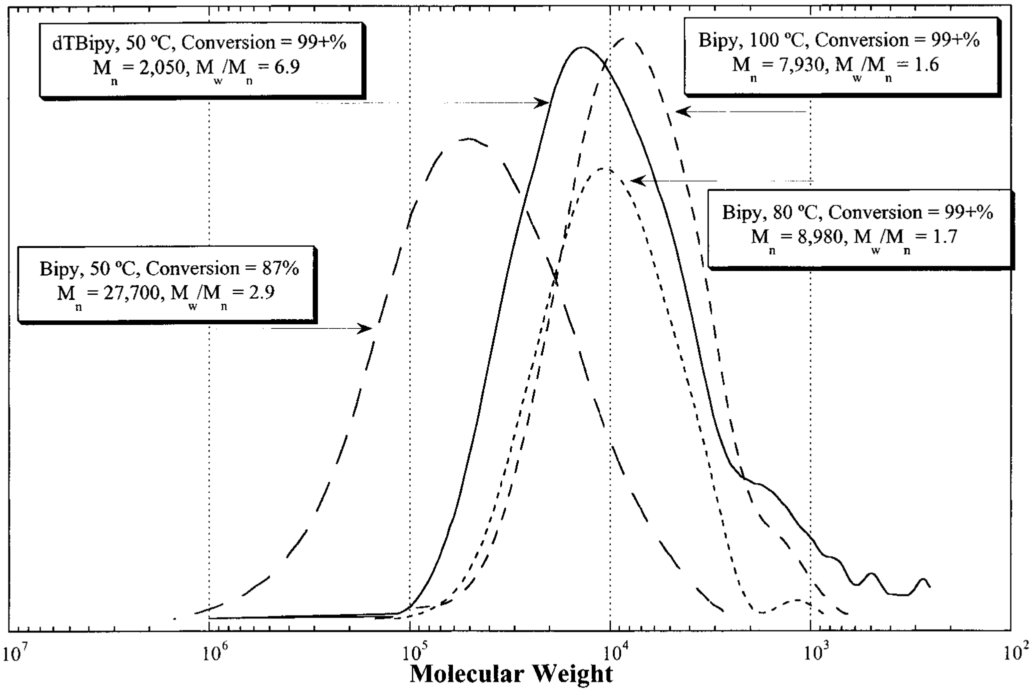


Figure 2. Comparison of SEC traces for the homopolymerization of BPEA by ATRP using copper(I)/Bipy at various temperatures. The result for copper(I)/dTBipy at 50 °C is added as a reference.

copper(I)/3Bipy catalyst (1 mol % relative to monomer) system and to perform the polymerization at 50 °C. However, both of these additives had only minor effects on the rate of polymerization, Figure 1, although the obtained molecular weights were slightly lower than when Bipy was used alone, Figure 3. These molecular weights are not entirely accurate, due to some branching in the polymers and the differences in the hydrodynamic volume of the BPEA polymers and the linear polystyrene used as calibration standards. Table 1 summarizes the characterization of the macromolecules prepared by ATRP of BPEA.

Determination of the proportion of B* in the polymers was performed by evaluation of the ^1H NMR spectra, Figure 4. The large doublet at 1.8 ppm has been assigned to B* and the mutliplet at 1.2 ppm to b.[20] It was possible to determine r by the following equation: $r = (x + B^* - 1)/(-\ln(B^*) + B^* - 1)$, where B^* is the proportion of B* groups in the polymer, and x is conversion.[20,21] The polymerizations catalyzed by Cu^IBr/Bipy at 50 °C provided essentially linear polymers, since no b units were observed. At higher temperatures (>100 °C), increasingly branched polymers were formed but this was accompanied by side reactions as evidenced by two new NMR signals at 3.5 and 4.9 ppm (vide infra).

The influence of temperature and ligand on r, the measure of the apparent R_p/R_d, can be seen in Figure 5. Recall that the maximum degree of branching of DB = 0.5 is obtained when $r = 2.6$ and that for a polymerization where the relative reactivities for the A* and B* sites are the same ($r = 1$), DB = 0.465. Since for

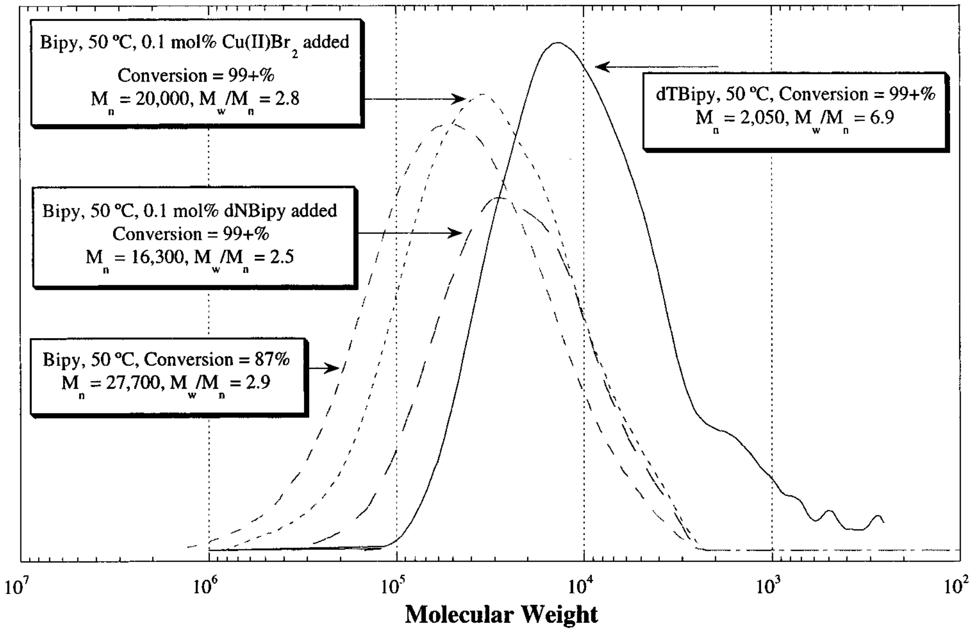


Figure 3. Comparison of SEC traces for effect of additive on homopolymerization of BPEA by ATRP using copper(I)/Bipy.

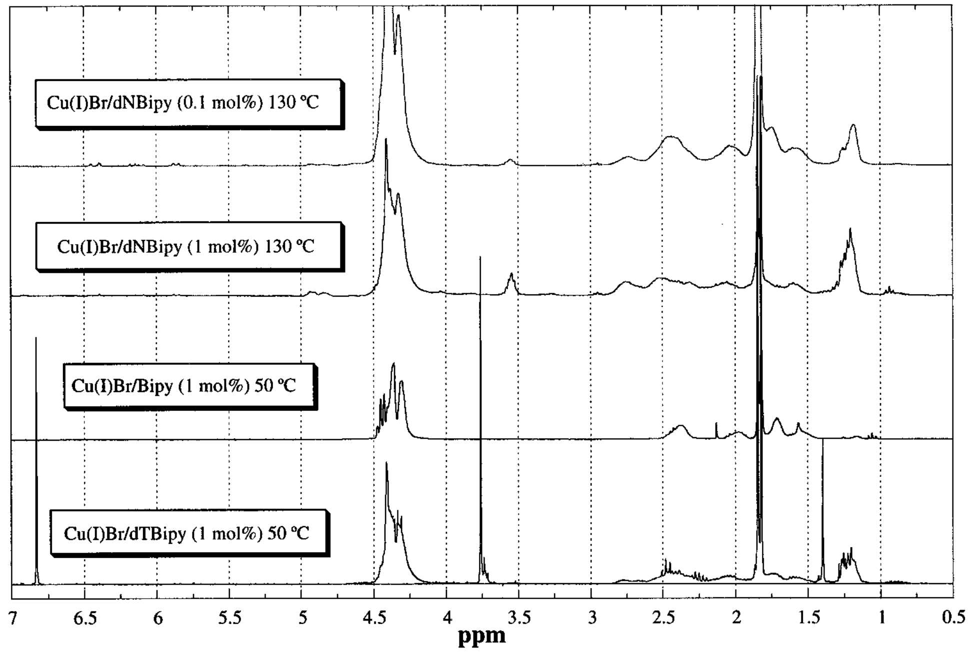


Figure 4. ^{1}H NMR of BPEA homopolymers prepared by ATRP.

Table 1. Characterization of the Homopolymerizations of BPEA by ATRP under Various Reaction Conditions

ligand	time (h)	temp (°C)	conversion	M_n[a]	M_w/M_n[a]	r
Bipy	2.5	50	0.87	27,710	2.9	124.0
	2.5	80	0.99	8,230	1.8	16.7
	2.5	100	0.99	7,930	1.6	7.2
dNBipy	100	100	<0.10			
		130	>0.95	4,240[b]	1.7[b]	2.5[b]
dTBipy	6	50	0.99	2,050	6.9	4.5
	23	100	0.95	8,300[b]	2.0[b]	3.65[b]

[a] Values based on SEC in THF against linear polystyrene standards. [b] Data obtained from precipitated sample.

the polymerization of BPEA, A* and B* are, chemically, nearly identical, r can be used as a measure of the ratio of propagation to deactivation, i.e., a measure of the number of monomer units added to an active center before deactivation.[20] The r values decreased with increasing temperature, Figure 5. This indicates that the average number of monomer units added per activation of A* or B* decreased when the solubility of the catalyst was higher (due to either an increase in the reaction temperature or by changing the ligand).

Although faster rates, and somewhat better control of the polymerization was obtained for the polymerizations using copper(I)/Bipy at higher temperatures, the high reaction temperatures were not desirable due to side reactions, which were clearly observed at 130 °C. In the ^{1}H NMR spectrum of the polymer obtained in the polymerization of BPEA at 130 °C, two new peaks were detected in the purified material, Figure 4. These peaks were centered at 4.9 and 3.5 ppm with the ratio of the peak areas being 1:2, respectively. These peaks are proposed to originate from the side reaction outlined in Scheme 3.

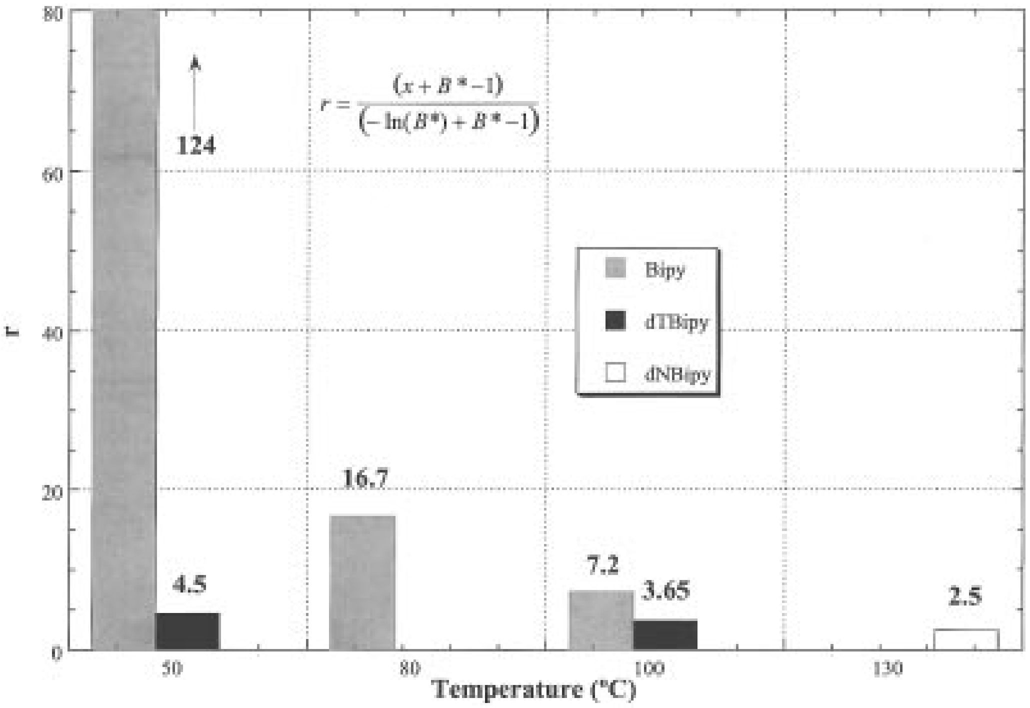
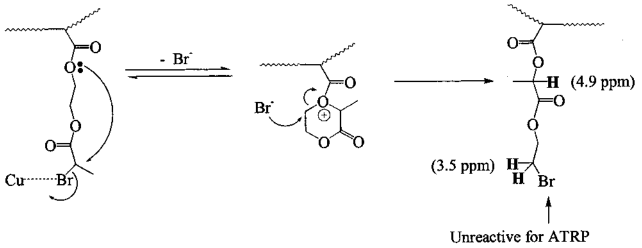


Figure 5. Evaluation of *r* vs temperature for various ligands. Values indicate *r* calculated for the final sample in the polymerization. $[Cu]_o$ = 55.6 mM (1% relative to BPEA).

Scheme 3



The reaction may be catalyzed by the copper halide, a weak Lewis acid. The peak at 4.9 ppm corresponds to the proton on the tertiary carbon, α to the ester, while the peak at 3.5 ppm corresponds to the protons geminal to the bromine atom. This is a significant side reaction since the resulting alkyl halide is not active toward copper(I) in ATRP. This effectively removes an active site from the macromolecule. Even at lower concentrations of copper (0.1 mol %) the peaks were still observed, but at lower relative concentrations.

Fortunately, the relative intensities of the two signals at 4.9 and 3.5 ppm decreased with reaction temperature. At 100 °C (dTBipy) there were small, yet still detectable signals present, while at 50 °C (dTBipy) they were below detectable levels. Thus, this side reaction could be avoided by performing the polymerization at lower temperatures.

The conclusions drawn from the experimental results indicate that the polymerization should be performed at as low a temperature as possible and that a suitable ligand should be used to control the solubility of copper(II) and, therefore, the rate of deactivation.

UV Spectroscopy

During previous polymerizations of AB* monomers by ATRP,[14,18] it was observed that the reaction medium turned from dark red to green almost instantly upon heating. For linear polymers prepared by ATRP, the polymerization is generally dark red in color. The solution turning green suggested that a significant proportion of the copper(I) had been converted to copper(II). Since the polymerizations proceeded to high conversions, the apparently high copper(II) levels must not completely suppress the polymerization. To quantify the amount of copper(II) present during the polymerization, a study of the concentrations of copper(I) and copper(II) in the reaction mixture was undertaken using UV/vis spectroscopy.

Benzene solutions of copper halide/dNBipy were prepared and analyzed; these were used as reference solutions to evaluate any changes in λ_{max}. The dark red copper(I) bromide solution displayed a peak around 400 nm corresponding to the charge transfer band of the bipyridyl with copper. A shoulder was observed at λ_{max} = 450 nm, ϵ = 640 M^{-1} cm^{-1}. Copper(II) bromide in benzene was dark green and displayed a peak at 525 nm, ϵ = 730 M^{-1} cm^{-1}, and at 700 nm, ϵ = 220 M^{-1} cm^{-1}.

The next solution studied was copper(I)/dNBipy dissolved in methyl 2-bromopropionate ($[Cu(I)\ Br]_o$ = 2.75 mM), Figure 6. This compound was chosen so as to mimic the B* group in BPEA. The solution of copper(I) bromide/dNBipy was originally dark red but turned to a dark green color within 15 min at room temperature. Analysis of the UV/vis spectrum showed the formation of a peak at 750 nm. Subsequent analysis of a copper(II) bromide/dNBipy solution (λ_{max} = 750 nm, ϵ = 380 M^{-1} cm^{-1}) showed that this peak was due to copper(II).[35] The amount of copper(II) formed was greater than 20% of the original copper(I), after *less than an hour at room temperature*. This result indicates that a high concentration of radicals was produced, leading to irreversible termination between radicals, and the production of relatively high concentrations of copper(II). This also means that 0.01 mol % of methyl 2-bromopropionate was consumed by the formation of the radical termination products.

p-(Chloromethyl)styrene (CMS) was also used as a medium for Cu^I Cl/dNBipy to see if copper(II) was

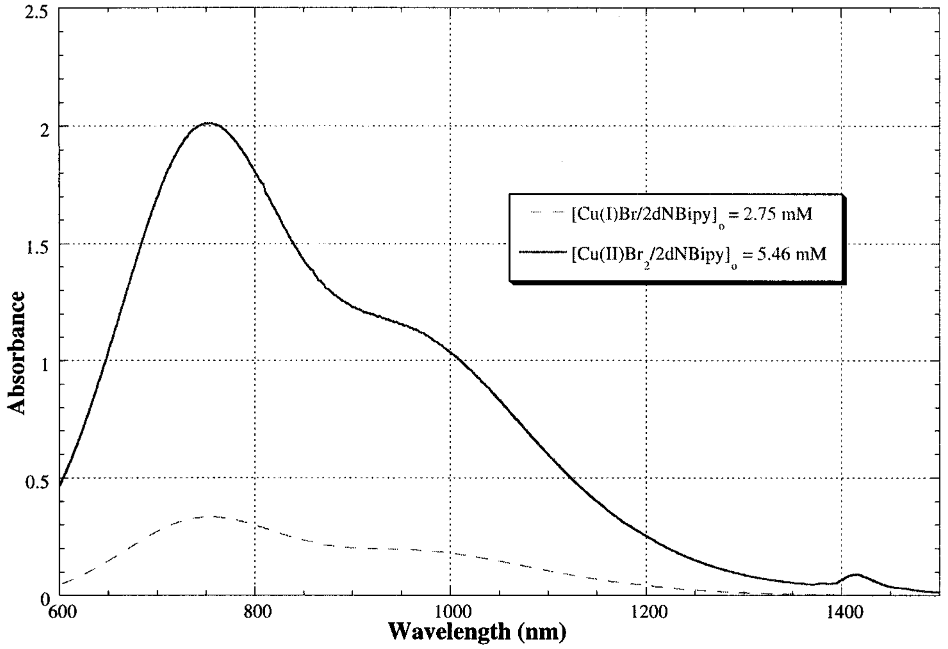


Figure 6. UV/vis spectra of reaction mixture of copper(I) and copper(II) bromide/dNBipy in methyl 2-bromopropionate at room temperature.

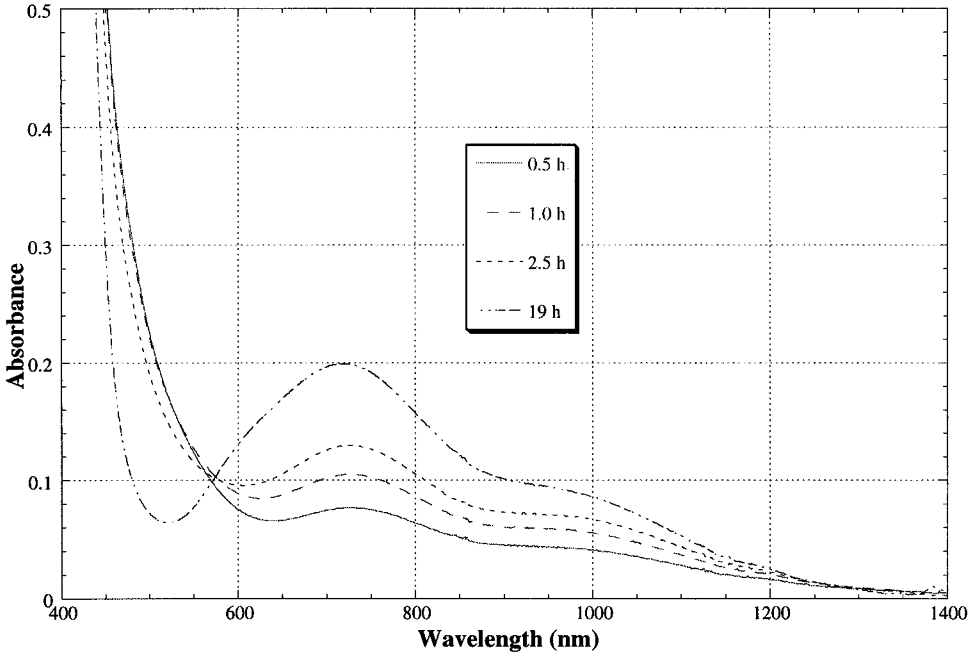


Figure 7. UV/vis spectra of reaction mixture of copper(I) chloride in *p*-(chloromethyl)styrene at various times at room temperature. $[Cu(I)]_o = 3.03$ mM.

formed for this monomer. Copper(II) was formed but at a slower rate. This reduction in rate was attributed to two factors: the higher bond dissociation energy of the C−Cl bond, and the relatively lower stability of primary vs secondary radicals. Figure 7 shows the UV/vis spectra of the copper(I)/CMS solution at various times. The copper(I) peak is overwhelmed by the absorption due to CMS (<600 nm). However, an isobestic point is clearly discernible at 560 nm indicating that there was a clean consumption of copper(I) to form the copper(II) (CMS: $\lambda_{max} = 700$ nm, $\epsilon = 180$ M^{-1} cm^{-1}). After 19 h, *at room temperature,* the amount of copper(II) present approaches 20% of the original copper(I) chloride.

The self-condensing vinyl polymerization of 2-((2-bromopropionyl)oxy)ethyl acrylate, BPEA, by atom transfer radical polymerization, was highly dependent upon the relative concentration of copper(II). It has also been shown that even at room temperature, the activation of an alkyl halide to a radical occurred. When ATRP is used to prepare linear chains, i.e., the polymerization of conventional monomers, the activation of the alkyl halide, and subsequent polymerization, was usually slow due to the low initiator concentration (≤0.1 M), as compared to SCVP (bulk, ~10 M). Since the concentration of the alkyl halide, in SCVP, was so high, the initial rate of radical formation was faster than in the synthesis of linear polymers by ATRP, eq 2. Because the initial rate of radical formation was faster, the concentration of radicals was higher, leading to an increased amount of termination, eq 3. In fact, the initial rate of termination could be nearly 4 orders of magnitude higher in

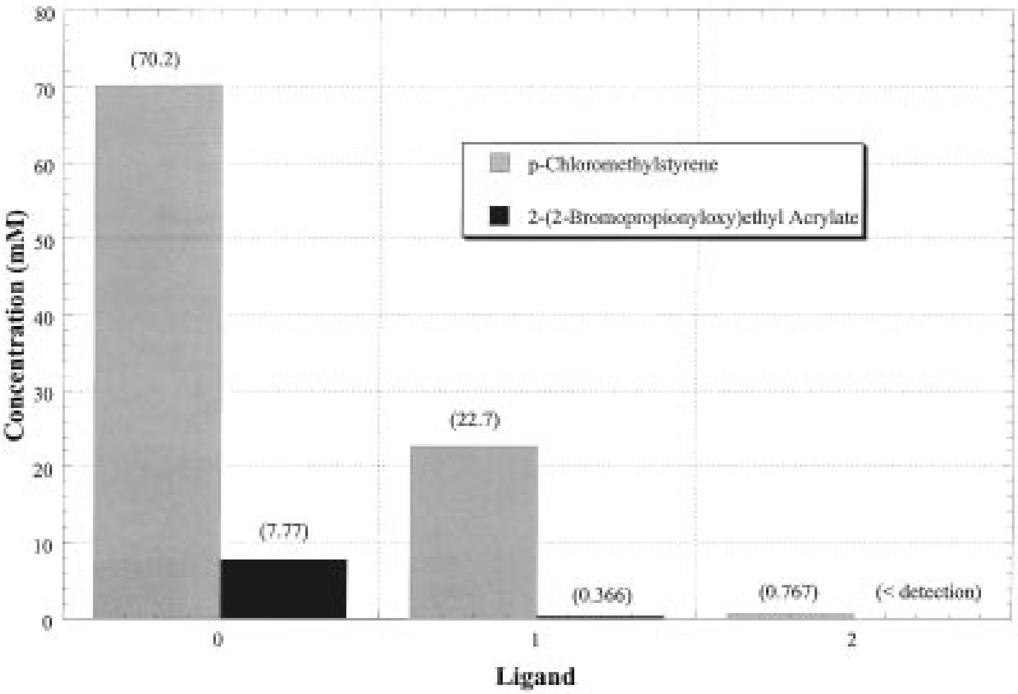


Figure 8. Concentration of saturated solutions of copper(II)/ligand catalysts in *p*-(chloromethyl)styrene or 2-((2-bromopropionyl)oxy)ethyl acrylate at room temperature. Values in parentheses are millimolar concentrations.

SCVP than in conventional polymerizations by ATRP.

$$[R^\bullet] = k_a[\mathrm{R{-}X}][\mathrm{Cu(I)}] \tag{2}$$

$$R_t = k_t[\mathrm{R}^\bullet]^2 \tag{3}$$

ATRP allows for the control of radical polymerizations by using a psuedoequilibrium between the active and dormant species to lower the concentration of radicals (to levels of $[\mathrm{R}^\bullet] = 10^{-7}-10^{-8}$ M), so that the amount of termination in the polymerization is reduced to levels which are below detection. This psuedoequilibrium is an example of the persistent radical effect, previously described by Fischer.[36] In the persistent radical effect, the concentration of active radicals is kept low by reaction of the radical with a compound which can reversibly deactivate that radical. In the case of ATRP, the deactivating compound is the higher oxidation state metal, i.e., copper(II) halide.

Normally, in the preparation of linear polymers by ATRP, the amount of copper(II) that is needed to keep the active radicals at low concentrations (10^{-7} M) is only a small fraction of the copper that is added to the polymerization system. However, when the amount of initiator and, consequently, the concentration of radicals are dramatically increased, as in SCVP by ATRP, much higher proportions of copper(II) are needed to lower the concentration of radicals in the polymerization system.

When ligands are used which completely solublize the copper salts, all of the copper(II) is kept in solution, which allows for fast deactivation of the propagating radical. But, in SCVP, as a consequence of the higher proportion of copper(II) relative to copper(I), the polymerization becomes extremely slow. This reduction in rate is a result of the rate of polymeization being proportional to [Cu(I)]/[Cu(II)] (eq 1). Therefore, if one can limit the solubility of the copper(II) in the reaction medium, it is possible to have deactivation but still maintain relatively fast rates of polymerization. By careful choice of the ligand, it was possible to vary the solubility of the copper(II) in solution and, therefore, the resulting structure of the polymer. To quantify the amount of copper(II) in solution, saturated copper(II) solutions were prepared, and the concentration of copper(II) in solution was determined by UV/vis, Figure 8. Solubilities and UV spectra of $CuBr_2$/2dNbipy are affected by CuBr/2dNbipy. Therefore, the concentrations of copper(II) species discussed in the text and illustrated in Figure 8 may not fully correspond to the real polymerization systems and should be viewed qualitatively.

Generally, the solubility of the complexes followed the trend dNBipy > dTBipy > Bipy and overall, CMS > BPEA. The solubility of the catalyst increased with increasing alkyl chain length. The reason for the higher solubility in CMS was not clear.

Conclusions

The rate of polymerization can be controlled by adjusting the ratio of copper(I)/copper(II), as higher concentrations of copper(II) allow for faster deactivation of the propagating radical and, thus, slower polymerizations. The ratio of copper(I)/copper(II) was adjusted by changing the ligand coordinated to copper; the solubility of copper increased in the following order: Bipy < dTBipy < dNBipy. In the systems where copper(II) was highly soluble, i.e., dNBipy, the polymerization was observed only at high temperatures.

By increasing the temperature of the polymerization, it was possible to enhance the rate of polymerization for all catalyst systems. Also, the degree of branching was observed to increase with temperature for a given catalyst system, e.g., copper(I)/Bipy. However, at temperatures higher than 100 °C, a side reaction was observed when using the copper(I)/dNBipy catalyst.

Finally, the structure of the polymer was controlled by varying the solubility of copper(II) in the reaction medium. For systems with a low copper(II) concentration, the deactivation of the propagating radical became slower, allowing for multiple monomer units to add to active centers before deactivation. An extreme example of this was the polymerization of BPEA using copper(I) bromide/Bipy at 50 °C; the polymerization appears to behave similarly to a redox-initiated polymerization. The high r value for this polymer, $r = 124$, indicated that the final polymer was essentially linear. On the contrary, the low r values for dNBipy at 130 °C ($r = 2.5$, DB = 0.5), Bipy at 100 °C ($r = 7.2$, DB = 0.46), or dTBipy at 50 °C ($r = 4.5$, DB = 0.49) suggested that highly branched polymers were prepared in these systems. Thus, it was demonstrated that the architecture of the polymer can be controlled by choosing the appropriate ligand and/or reaction temperature.

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