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Studying the Fundamentals of Radical Polymerization Using ESR in Combination with Controlled Radical Polymerization Methods

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Summary: Electron spin resonance (ESR) spectroscopy can contribute to understanding both the kinetics and mechanism of radical polymerizations. A series of oligo/poly(meth)acrylates were prepared by atom transfer radical polymerization (ATRP) and purified to provide well defined radical precursors. Model radicals, with given chain lengths, were generated by reaction of the terminal halogens with an organotin compound and the radicals were observed by ESR spectroscopy. This combination of ESR with ATRPs ability to prepare well defined radical precursors provided significant new information on the properties of radicals in radical polymerizations. ESR spectra of the model radicals generated from *tert*-butyl methacrylate precursors, with various chain lengths, showed clear chain length dependent changes and a possibility of differentiating between the chain lengths of observed propagating radicals by ESR. The ESR spectrum of each dimeric, trimeric, tetrameric, and pentameric *tert*-butyl acrylate model radicals, observed at various temperatures, provided clear experimental evidence of a 1,5-hydrogen shift.

Keywords: atom transfer radical polymerization (ATRP); ESR/EPR; kinetics (polym.); radical polymerization

Introduction

Electron Spin Resonance (ESR) spectroscopy can contribute to understanding both the kinetics and the mechanism of radical polymerizations.[1–5] Propagation rate constants (k_p) of various kinds of monomers have been estimated using ESR spectroscopy.[1,5] Indeed ESR is one of the most effective methods for estimating values for k_p and it is a mutually complementary method to the Pulsed Laser Polymerization (PLP) method. Usually equation (1), and its integrated form (2), have been used to calculate k_p by ESR.

$$R_p = -\frac{d[M]}{dt} = k_p[P_n^\bullet][M] \qquad (1)$$

$$\ln\frac{[M_1]}{[M_2]} = k_p[P_n^\bullet](t_2 - t_1) \qquad (2)$$

The advantage of ESR is that the value of $[P_n^\bullet]$ in these equations can be determined from the observed ESR spectra of propagating radicals. Detailed analysis of the spectra provides information, not only on radical concentration, but also on the structure and other physicochemical properties of the radicals. Furthermore, steady state radical concentrations can be confirmed from the spectra. On the other hand, the ESR method makes two important assumptions: one is that we observe the propagating radical with sufficiently long chain length and the other is that we observe real propagating radicals.

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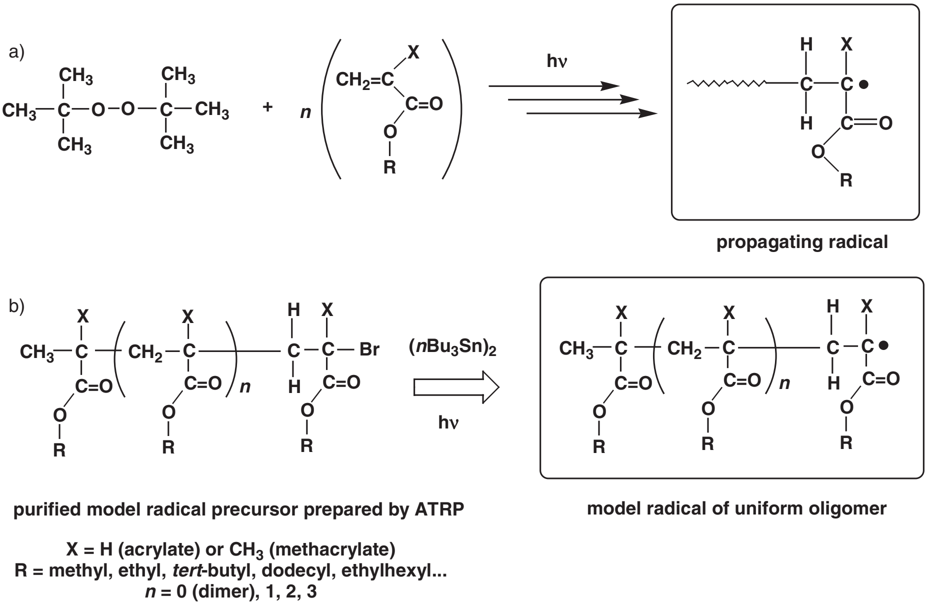
Atom transfer radical polymerization (ATRP) is one of the most widely applied polymerization techniques in the field of controlled/living radical polymerization.[6,7] The polymers formed in ATRP contain terminal carbon-halogen bonds. Giese *et al.* (Scheme 1)[8] has reported that these bonds can be homolytically cleaved by reaction with organotin compounds. Accordingly, various radicals that model the active end groups in an ATRP can be formed from the corresponding precursors prepared by atom transfer radical addition (ATRA) and ATRP. The generated radicals can be studied by ESR spectroscopy. Systematic variation of the chain length and composition of polymeric radical precursors elucidates the effect of chain length and penultimate units on the ESR spectra of the formed radicals.[9] It was previously reported,[10] that the ESR spectra of propagating *tert*-butyl methacrylate radicals show chain length dependency.

In another study on conventional radical polymerizations of acrylates, large amounts of mid-chain radicals were detected by ESR spectroscopy and it was suggested that the terminal propagating radicals had rearranged to form a mid-chain radical.[2] In that study,[2] and in other reports,[11–16] it was suggested that the formation of mid-chain radicals occurred via a 1,5-hydrogen shift, but no mechanism was proposed and there was no clear experimental evidence for the "1,5-hydrogen shift" reaction. Possibilities of a 1,7-, a 1,9-hydrogen shift, or some other reaction e.g. intermolecular chain transfer remained. This ESR study of model radicals generated from radical precursors prepared by ATRP provided significant information on the rearrangement and allows a conclusion to be reached. Accordingly, ESR spectroscopy in combination with ATRP has given an unambiguous proof of several reactions that are involved in radical polymerization.

In this research work, a series of uniform oligomeric and polymeric radicals, with various chain lengths, were prepared to serve as models of propagating radicals. The model radicals were generated from oligomers prepared by ATRP and purified by column chromatography; each uniform oligomer was a pure compound with an



Scheme 1.
Generation of propagating radicals (a) and oligomeric model radicals (b). ESR spectra of methacrylate showed chain length dependence. ESR spectra of acrylate radicals show clear proof of a 1,5-hydrogen shift.

exact molecular weight. This systematic study using uniform oligomers with various chain lengths would provide a clearer perspective in the study of propagating radicals.

In this article, two examples of the application ESR to conventional radical polymerizations, especially to both kinetics and mechanism, based on materials prepared by controlled/living radical polymerizations will be demonstrated. The first example is the estimation of the effect of chain length on propagating radicals. The second is the detection of chain transfer reactions on propagating radicals in the polymerization of *tert*-butyl acrylate.

Chain Length Dependence

ESR Spectra of Propagating Radicals of *tert*-Butyl Methacrylate (*t*BMA)

When a mixture of a monomer and a radical initiator is heated, or photo-irradiated, in an ESR sample cell, propagating radicals are formed and polymerization proceeds (Scheme 1a, $X = CH_3$). Well-resolved spectra of propagating radicals of *tert*-butyl methacrylate (*t*BMA) have been detected in such polymerization systems at various temperatures; as shown in Figure 1, 16-line spectra were clearly observed. The spectroscopic feature of the spectra showed a clear temperature dependence which can be interpreted by a hindered rotation model of two stable conformations.[2,5,8] The intensity of the inner 8 lines increased with increasing temperature, indicating that there are two exchangeable conformations whose existence have been shown by elucidation of ESR spectra of methacrylates. [2,5,8]

At 150 °C, the intensity of the inner 8 lines increased and the ESR spectrum can be interpreted as a single conformation, indicating that the energy difference between the two conformers is small. The observed ESR spectrum of propagating radicals of *t*BMA at 150 °C is shown in Figure 2a along with the simulated spectrum. The spectrum is completely simulated

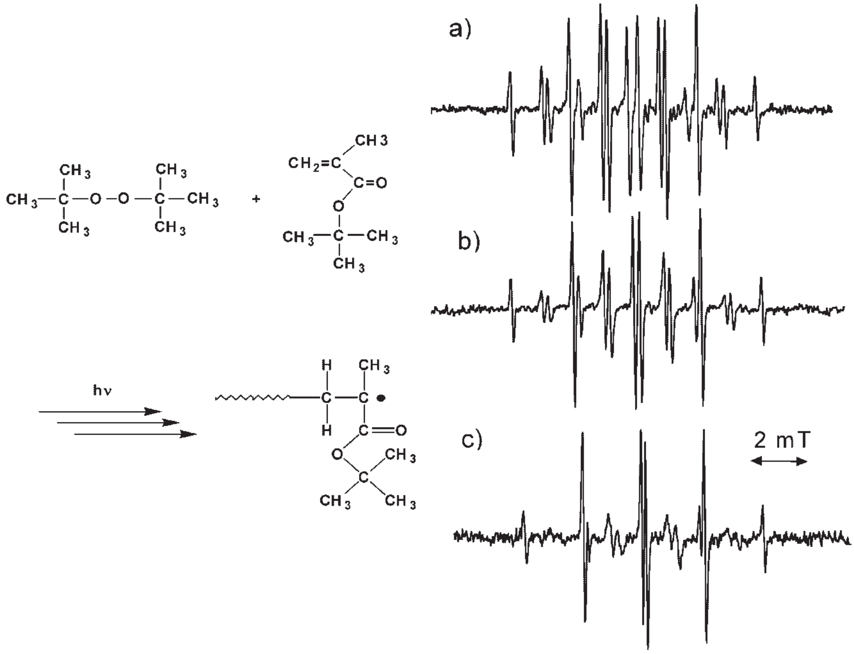


Figure 1.
Polymerization scheme and observed ESR spectrum of propagating radical of *t*BMA in radical polymerizations at 150 °C (a), 90 °C (b), and 30 °C (c).

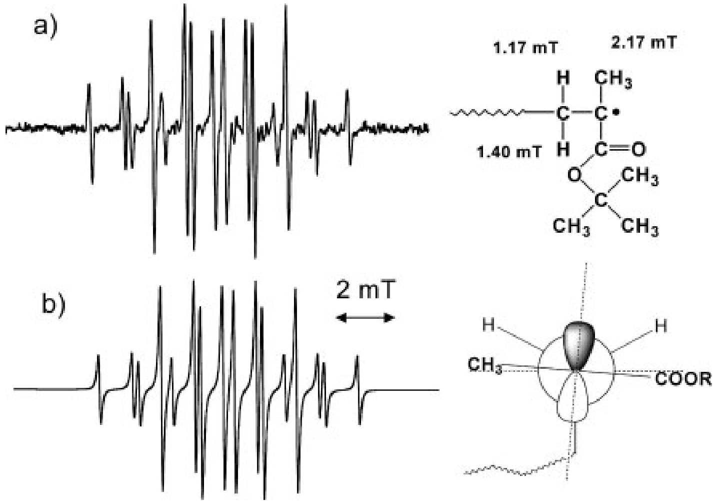


Figure 2.

Observed ESR spectrum of propagating radical of *t*BMA in radical polymerizations at 150 °C (a) along with its simulation (b). Values of hyperfine splitting constants are shown in the Figure. A Newman projection of one of stable conformer is also shown.

using hyperfine splitting constants of 1.40 mT for one methylene proton (1:1 doublet), 1.16 mT for the other one proton (1:1 doublet), and 2.17 mT for three equivalent methyl protons (1:3:3:1 quartet) as shown in Figure 2b.

A characteristic result is that different hyperfine splitting constants may be estimated for the two methylene protons. This means that the rate of rotation of the end radical is not fast enough to make the methylene protons equivalent within the time scale of the ESR measurement. Thus, it leads to a 16-line spectrum ($2 \times 2 \times 4$). If the two β-methylene protons were equivalent, the total number of splitting lines would be 12 (4 (CH_3–) × 3 (–CH_2–)). This suggests the presence of a propagating radical with a long chain that hinders the rotation of the terminal bond to generate the 16-line spectrum and also another oligomeric radical which may show a 12-line spectrum.

If we could observe the ESR spectra of radicals with controlled chain length, chain length dependent phenomena could be precisely examined. In order to clarify the phenomena, model radical precursors were prepared by the ATRP technique. ATRP can provide polymers with controlled molecular weights and low polydispersity, and the resulting polymers have preserved terminal carbon-halogen bonds.[6,7] Model radicals of propagating chains with given chain length could be generated when the carbon-halogen bonds are cleaved homolytically by reaction with organotin compounds, (Scheme 1b, $X = CH_3$).[6,7]

Differentiating Between Chain Lengths of Observed Radicals

First, a mixture of oligomers containing 2–7 monomer units ($P_n = 2–7$) was prepared by ATRP and the dimeric model radical precursor was isolated and purified from the mixture. Preparation and purification were successful and the dimeric model radical was generated from the precursor. Clear and well-resolved ESR spectra of the model radical were observed at various temperatures. The ESR spectrum of the radicals observed at 150 °C showed a 12-line spectrum, as shown in Figure 3a. The two β-methylene protons are almost equivalent in dimeric radicals at such high temperature. This finding indicates that rotation of the radical chain end is too fast

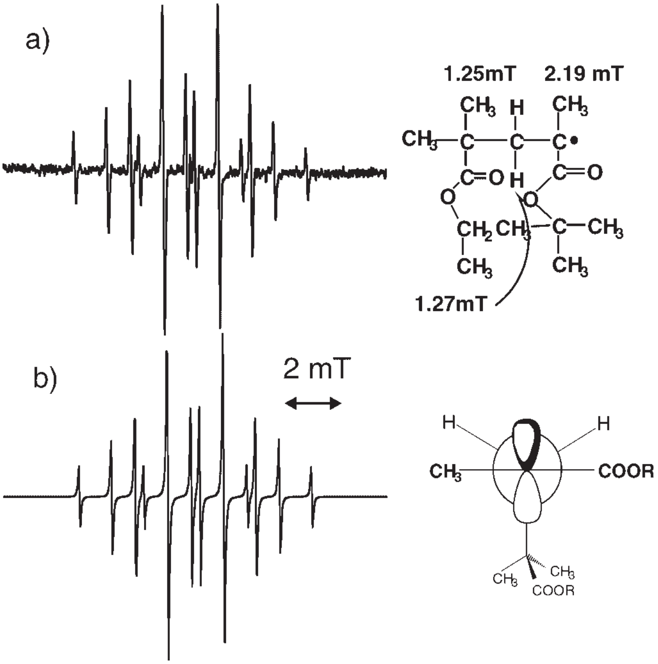


Figure 3.
Observed ESR spectrum of dimeric model radical of *t*BMA at 150 °C (a) along with its simulation (b). Values of hyperfine splitting constants are shown in the Figure. A Newman projection of one of the stable conformers is also shown.

to detect differences in methylene protons on the time scale of ESR spectroscopy.

In order to estimate the critical chain length which would show splitting of 16-line spectrum, model radical precursors with degrees of polymerization (P_n) of 30, 50, and 100 were prepared by ATRP. Polymers with targeted molecular weights and low polydispersities were obtained. ESR spectra of radicals generated from these precursors were observed at various temperatures. Although the lifetime of the model radicals were very short at 150 °C, clear and well-resolved spectra were observed. These spectra showed similar temperature dependence to that shown in Figure 1. In the case of $P_n = 100$, the intensity of the inner 8 lines increased with increasing temperature, and seems to coalesce into a single line at 150 °C. Similar ESR spectra were observed in radicals from polymeric precursors with $P_n = 50$ and 30. The intensity of the inner 8 lines seems to coalesce more clearly to a single line at 150 °C. The ESR spectra seemed to be 12-line spectrum, but the 4 lines coalesced insufficiently, indicating that the rate of the rotation of the end radical is not sufficiently fast for the methylene protons to be detected as equivalent species on the time scale of the ESR experiment. The inner 4 lines of the 12-line spectrum begin to separate into two lines at $P_n = 30$, and the separation becomes larger with increasing P_n owing to the lowering of the rate of the rotation. The separation was more clearly observed in the propagating radical, indicating that mobility of the chain end radical is restricted.

A comparison of the ESR spectra of the dimeric radical (Fig. 3a), model radicals with $P_n = 100$, and radicals in a polymerization system at 150 °C is shown in Figure 4. The separation of the inner lines, P_n of the propagating radical indicate that the degree of polymerization is higher than 100. When the values of hyperfine splitting constants measured from these spectra, were plotted against chain length, they seemed to show

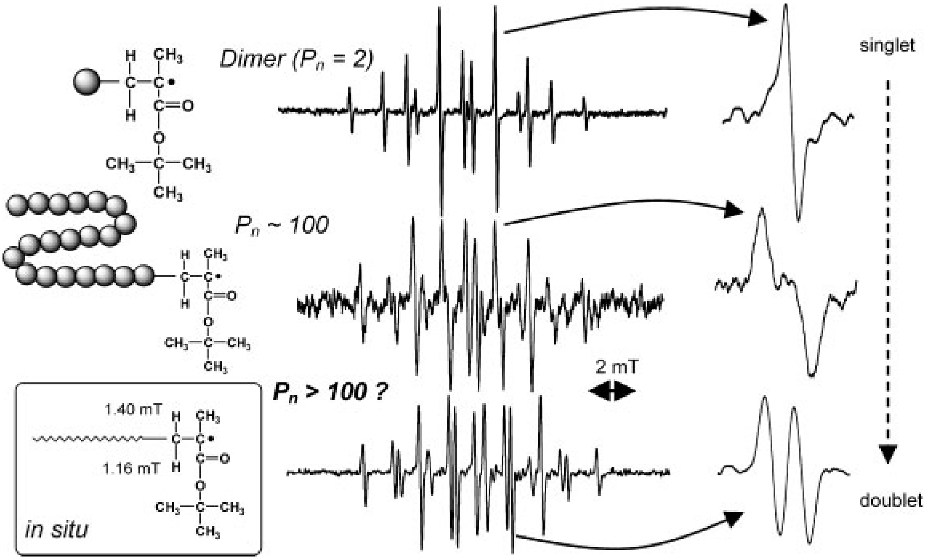


Figure 4.
Comparison of ESR spectra of radicals with various chain length at 150 °C. Dimeric model radical, model radical with $P_n = 100$, and radicals in a radical polymerization (propagating radical). Characteristic lines were enlarged on the right hand side.

nearly linear correlation between hyperfine splitting constants and chain lengths in the range up to $P_n = 200$. Molecular weight (M_n) of the isolated polymers from polymerization system was determined to be 30000 ($P_n = 210$) by size exclusion chromatography (SEC). The interpretation of the ESR spectra suggests that they correspond to ''long'' propagating radicals, and it is in agreement with SEC. Prior to these experimental results, ESR spectra and overall SEC results did not correlate. However, more experimental results are needed for a more comprehensive correlation of kinetic data with ESR spectra.

We can conclude that the 16-line spectrum in ESR measurements can be ascribed to ''polymeric'' radicals with more than 100 monomer units and that ESR spectroscopy has provided structural information on the propagating radicals at their chain ends.

Radical Migration during Polymerizations

tert-Butyl Acrylate (*t*BA)

ESR spectra observed in radical polymerization of acrylates are very different from those for methacrylates, even under almost identical conditions (Fig. 5a). Accordingly, it is difficult to interpret the spectrum to be that of propagating radicals. Spectroscopic changes were observed in ESR spectra during the solution polymerization of *tert*-butyl acrylate (*t*BA) as shown in Figure 5. A 6-line spectrum or a doublet of triplets with narrow line width (Fig. 5c) was observed at −30 °C. This spectrum can be reasonably assigned to a propagating radical with two β-methylene protons (1:2:1 triplet) and one α-proton (1:1 doublet). At 60 °C, a totally different 7-line spectrum with broader line width was observed (Fig. 5a). While it was much easier to observe the latter spectrum than the former one traces of the 6-line spectrum can be seen in the spectrum at 60 °C, but the amount of the species giving rise to the 6-line spectrum is 1000 times lower than that of the source of the high temperature spectrum. At −10 °C, overlapped spectra of the first and latter spectra were observed (Fig. 5b). Signal intensity due to higher temperature spectrum with broader line width increased with time. These results suggest that the spectrum observed at

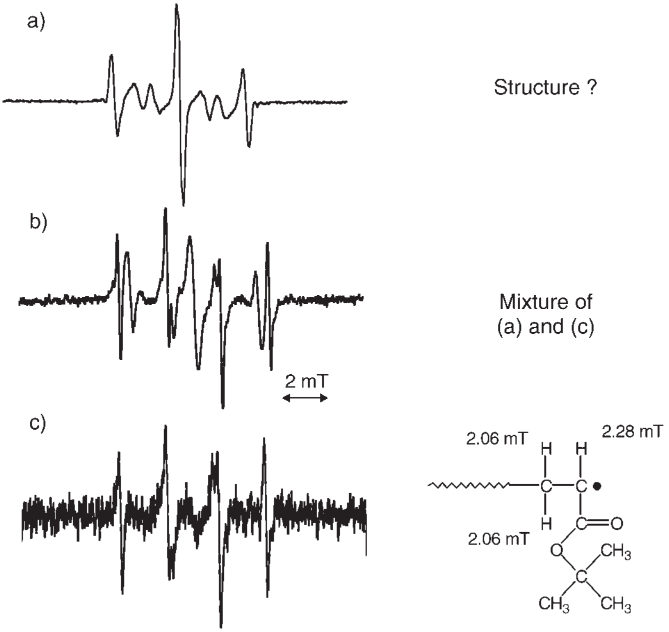


Figure 5.
ESR spectra observed in radical polymerization of *t*BA initiated with *t*BPO under irradiation at 60 °C (a), −10 °C (b), and −30 °C (c) in toluene.

−30 °C is converted to the spectrum observed at 60 °C. Some reaction should be responsible for such a change. Similar findings were observed for other acrylates, e.g. methyl acrylate, dodecyl acrylate, phenyl acrylate, and others. Two potential explanations for this change had been considered. One is a chain-length dependence of the spectra and the other is chemical transformation (e.g. transfer). These possibilities were examined by analysis of ESR spectra of model radicals with various chain lengths generated from polymeric radical precursors prepared by ATRP.[2–4] The possibility of chain length dependent change was discarded after examination of results from experiments using radical precursors of poly*t*BA with controlled chain lengths (Pn = 15, 50, and 100). The change from low temperature spectrum to the one at higher temperature was clearly observed even in model radical systems with fixed chain lengths. The possibility of chemical transformation remained. The ambiguity was resolved by ESR spectroscopy of several purified oligomeric model radical precursors.

SEC elution diagrams of model radical dimer, trimer, tetramer, and pentamer precursors are shown in Figure 6 along with that of a mixture. As shown in the figure, separation and purification of the oligomers was successful. Model radicals

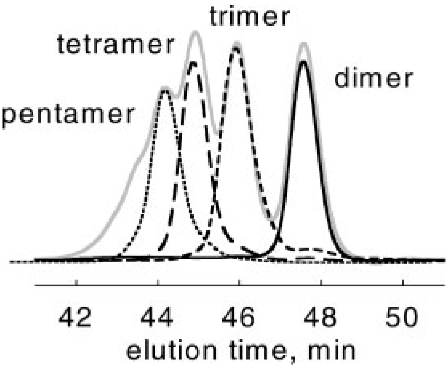


Figure 6.
SEC elution diagram of purified dimer, trimer, and tetramer of *t*BA as uniform radical precursor along with that of mixture of oligomers.

with clearly defined structures were generated by the reaction of the corresponding alkyl bromides (H-ethyl acrylate (EA)-*t*BA-Br, H-EA-*t*BA-*t*BA-Br, H-EA-*t*BA-*t*BA-*t*BA-Br, H-EA-*t*BA-*t*BA-*t*BA-*t*BA- Br) with an organotin compound under irradiation.

The resulting radicals had structures of hydrogenated radicals, i.e., H-EA-*t*BA•, H-EA-*t*BA-*t*BA•, H-EA-*t*BA-*t*BA-*t*BA•, and H-EA-*t*BA-*t*BA-*t*BA-*t*BA• respectively. Each of these radicals was investigated by ESR spectroscopy at various temperatures. Clear well-resolved spectra were observed and precise values for hyperfine splitting constants can be determined from the spectra. The ESR spectrum of the dimeric radical (H-EA-*t*BA•) showed a doublet of triplets in each spectrum at various temperatures within the range of −30 to +150 °C. The doublet and triplet were reasonably considered to be due to the splitting from the α- proton and two equivalent β-methylene protons, respectively. Nothing happened to the dimeric radical even at higher temperatures. On the other hand, model trimeric and tetrameric radicals showed a clear irreversible temperature dependent change, as shown below.

In the case of the model trimeric radical (H-EA-*t*BA-*t*BA•), the ESR spectrum observed at −30 °C (Fig. 7a) was very similar to that of the dimeric radical. This spectrum is ascribed to a chain end radical as shown in the figure. ESR spectra were measured every 30 degree as the temperature was increased from −30 °C to 120 °C. As the temperature was raised, the spectrum gradually and irreversibly changed to a different one. Between 0 °C and 60 °C, two overlapping spectra were observed. The change was complete at 120 °C. The resulting spectrum, observed at higher temperatures, was totally different from that at lower temperatures (Fig. 7b). When a 1,5-hydrogen shift occurs, the radical should migrate from one end to the other end of the trimeric model radical as shown in Figure 7. The spectrum can be simulated using hyperfine splitting constants shown in the figure. The most important feature of this simulation is a small triplet (0.11 mT) that appears in each spectroscopic line. When this trimer was prepared by ATRP, ethyl 2-bromo propionate was used as the initiator and the initiator fragment was counted as first monomer unit. So, we only had an ethyl ester group at the other chain end. The presence of a small triplet clearly indicates that the radical is located on the first ethyl acrylate unit. Consequently, we can say that the radical migrated from one end to the other end of the trimer.

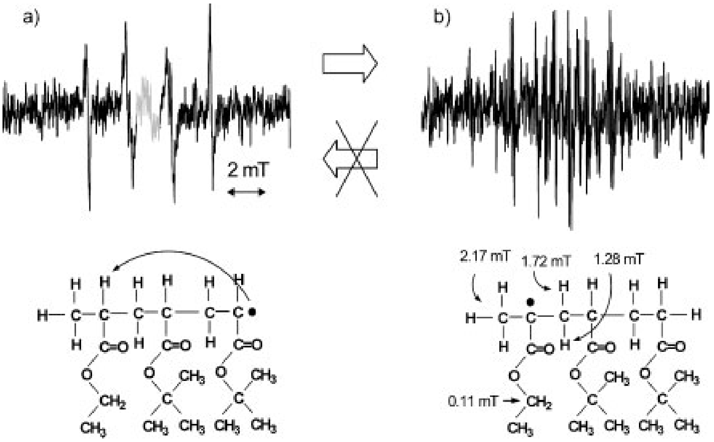


Figure 7.
ESR spectra of trimeric model radical (H-EA-*t*BA-*t*BA•) at −30 °C (a) and at +120 °C (b) with their estimated structures. Upon heating, an irreversible spectroscopic change occurred due to hydrogen abstraction.

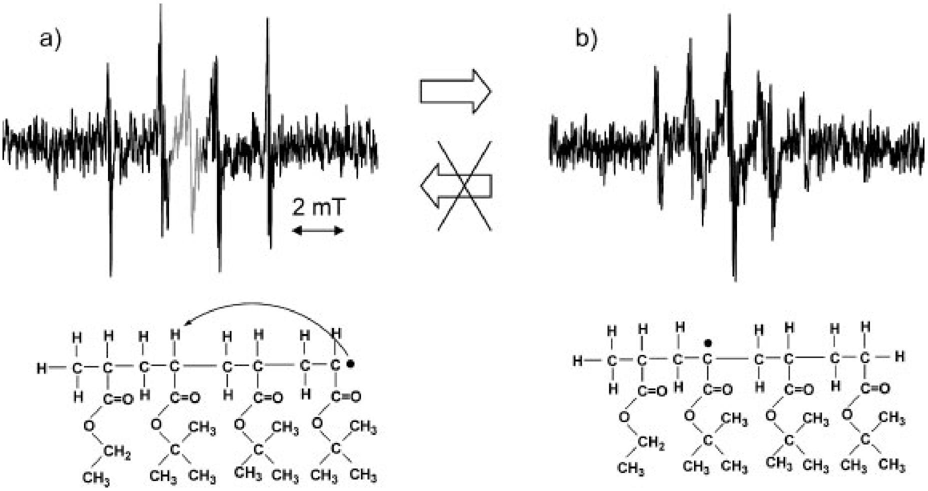


Figure 8.
ESR spectra of tetrameric model radical (H-EA-*t*BA-*t*BA-*t*BA•) at $-30\,^{\circ}$C (a) and at $+120\,^{\circ}$C (b) with their estimated structures. Upon heating, irreversible spectroscopic change occurred due to hydrogen abstraction.

A similar ESR study was done for the tetrameric model radical (H-EA-*t*BA-*t*BA-*t*BA•). The ESR spectra at $-30\,^{\circ}$C and $120\,^{\circ}$C are shown in Figure 8. The low temperature spectrum, observed at $-30\,^{\circ}$C, was very similar to those from the dimeric and trimeric model radicals. Similarly to the trimeric model radical, at higher temperatures an irreversible spectroscopic change took place. However the final spectrum was different from that of the trimeric model radical. In the case of a tetrameric model radical, a 1,5-hydrogen shift would cause transfer of a radical from the chain end to the first *t*BA unit, which is located two units away from the other end unit, through a six-membered ring structure (Figure 9). The transferred radical should have mid-chain type structure with methylene groups at both sides (H-EA-*t*BA(•)-*t*BA-*t*BA-H). The spectrum of the radical shown in Fig. 8b is attributable to such a mid-chain radical. These findings provide clear experimental evidence of a 1.5-hydrogen shift at the propagating chain end of acrylate radical polymerizations.

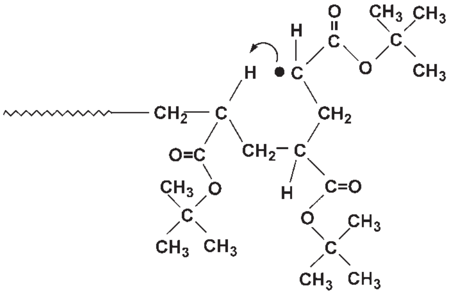


Figure 9.
1,5-Hydrogen shift of propagating radical of *t*BA.

A pentameric model radical was also generated and observed by ESR and a similar temperature dependent spectroscopic change to those seen in the case of the trimer and tetramer was observed. The resulting high temperature spectrum is very similar to those observed in polymeric acrylate radicals.

These findings strongly suggest that the mechanism of chain transfer reaction in an acrylate radical polymerization is a 1,5-hydrogen shift that occurs through a six-member ring structure. Formation of a six- member ring is a kinetically favored process and the transfer occurred from a secondary radical to form a thermodynamically more stable tertiary radical. An additional piece of information can be obtained from the result of the pentamer radical. Actually, the pentamer has one more chance for radical migration, from a mid-chain radical to the other chain end. However, this migration was not observed. The reason for this is unresolved.

Although there may be some minor contribution of intermolecular chain transfer, these systematic studies have provided a clearer perspective of the mechanism of the chain transfer reaction of propagating acrylate radicals. With increasing molecular weight, other factors also are becoming more important like conformation (rigidity), side group bulkiness and statistics. Further investigation will provide decisive proof of the mechanism.

Conclusion

Electron spin resonance (ESR) of a series of well defined radicals generated from oligomers prepared by atom transfer radical polymerization (ATRP) has provided significant new information on the properties of radicals in radical polymerizations, e. g. effect of chain lengths, dynamics, and reactivity (hydrogen transfer) of propagating radicals. Previously, it had been extremely difficult, even impossible, to obtain such information from ESR spectra during conventional radical polymerizations. Radical precursors of oligo- and poly-(meth)acrylates were prepared by ATRP and purified. Model radicals with given chain lengths were generated by reaction with an organotin compound and the radicals were observed by ESR spectroscopy. Model radicals of *tert*-butyl methacrylate with various chain lengths showed clear chain length dependent ESR spectra. Similar findings were also observed in cases of methyl methacrylate, *n*-butyl methacrylate, and benzyl methacrylate based radicals. These results will provide supporting information on the kinetics of radical polymerization. The ESR spectrum of dimeric, trimeric, tetrameric, and pentameric *tert*-butyl acrylate model radicals observed at various temperatures provided clear experimental evidence for a 1,5-hydrogen shift.

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