ESR spectroscopic studies directed at clarifying the fundamentals of radical polymerizations have been conducted. Optimization of measurement conditions allows direct detection of radicals in polymerization reactions and well-resolved ESR spectra can be obtained. The spectra provide information not only on the structure, properties, and concentration of radicals but also information on the initiating and propagating (oligomeric and polymeric) radicals in radical polymerizations. A combination of ESR and atom transfer radical polymerization (ATRP) provided significant new information on the properties of radicals in radical polymerizations, e.g., dependency of chain length, dynamics, and reactivity (hydrogen transfer) of propagating radicals. Previously, it has been extremely difficult, even impossible, to obtain such information from ESR spectra during conventional radical polymerizations. To overcome this difficulty radical precursors of oligo- and poly(meth)acrylates were prepared by ATRP and purified. Model radicals, with given chain lengths were generated by reaction of the well-defined radical precursors with an organotin compound and the radicals were observed by ESR spectroscopy. tert-Butyl methacrylate (tBMA) radicals 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. These results will provide supporting information on the kinetics of radical polymerization. For acrylates, each ESR spectrum of dimeric, trimeric, tetrameric, and pentameric tert-butyl acrylate (tBA) model radicals observed at various temperatures provided clear experimental evidence of the 1,5-hydrogen shift.

Introduction

ESR is the most powerful tool for investigations of radical species in radical polymerizations. When well-resolved spectra can be observed, the spectra provide information not only on the structure, properties, and concentration of radicals but also information on the initiating and propagating (oligomeric and polymeric) radicals in radical polymerizations [1-16]. Direct detection of propagating radicals in radical polymerization by ESR spectroscopy has been very difficult, mainly due to a combination of the labile nature and the extremely low concentration of the propagating radicals. Nevertheless well-resolved ESR spectra in the radical polymerizations of styrene and its derivatives, diene compounds, methacrylates, and vinyl esters were studied in benzene or toluene solution under normal polymerization conditions (Fig. 1) [5-7, 10, 12].

An example of an ESR spectrum of the propagating radicals of methyl methacrylate (MMA), observed during a polymerization reaction, is shown in Figure 2. It is well-resolved and shows the characteristic feature of hyperfine structures. Since values of hyperfine splitting constants were determined very precisely from the spectrum, it was able to be reasonably well simulated as the corresponding propagating radical, also shown in the Figure. Based on these spectra, kinetic analysis, especially for estimation of propagating rate constants \( k_p \) of the monomers, was performed. ESR spectroscopy was successfully applied to quantify radical concentration in the polymerizations. However, the direct detection method did not reveal many points that are very significant in radical polymerization chemistry. For example, the life of propagating chain is not known. In the estimation of \( k_p \), chain length of the observed propagating radicals is considered to be long enough for estimation of \( k_p \). However, there has been no clear experimental information on the actual chain length of the propagating radicals observed by ESR. The chain length was just hypothesized to be "long enough". In order to detect the well-resolved spectra, initiator concentration in some ESR experiments was higher than in usual radical polymerizations. Under such conditions, the chain length of the propagating radicals could be shorter than those formed under normal conditions. The chain length of the propagating radicals in ESR spectra can be estimated by measuring size exclusion chromatography (SEC) after ESR experiments. However, the resulting molecular weights, even if they were high enough, do not guarantee ESR detection of radicals with high molecular weights, because detection of shorter chain radicals is much easier than that of longer chain radicals. Therefore, the effect of the chain length of the propagating radicals in the polymerizations should be examined carefully. Moreover, it is extremely difficult to investigate copolymerization systems by the direct detection method. Copolymerization is a very important technique in radical polymerizations and it contains various kinds of propagating chain ends due to, so-called, penultimate unit effects. These problems have not yet been resolved but the development of controlled radical polymerization techniques, especially atom transfer radical polymerization (ATRP), enables us to solve some of these problems.

ATRP is one of the most widely applied polymerization techniques in the field of controlled/living radical polymerization. ATRP allows the preparation of a wide range of polymeric materials with controlled molecular weights and well-defined architectures [17-26]. The polymers formed in ATRP most frequently contain terminal carbon-halogen bonds. Giese et al. has reported that these bonds can be homolytically cleaved by reaction with organotin compounds [27]. Accordingly, various radicals that model the end groups in an ATRP can be formed from the corresponding precursors prepared by atom transfer radical addition (ATRA) and ATRP and the generated radicals can be studied by ESR spectroscopy. For example, polymeric (meth)acrylates with various chain lengths can be prepared as radical precursors by ATRP. Variation of the chain length of these polymeric radical precursors elucidates of the affect of chain length on the ESR spectra of the formed radicals.

The investigations of radical reactions are difficult without using model reactions. Poly(meth)acrylates with various chain lengths can be prepared by ATRP and propagating radicals, with various known chain lengths, can be generated from these model precursors. The ESR spectra of these model radicals at various temperatures are expected to show chain length dependence effects. ESR spectra of propagating radicals of methacrylates observed in situ show a clear temperature dependency due to the dynamics of chain ends [5]. This phenomenon can be applied to study chain length dependent spectroscopic variation using model radicals. This method can also be applied to investigate chain transfer reactions.
for propagating acrylate radicals.

**Direct ESR Detection of Propagating Radicals**

**Progresses of Techniques on the Detection of ESR Spectra of Radicals during Polymerizations**

Many technical problems associated with direct measurement of ESR signals from propagating radicals have been overcome. Direct detection of propagating radicals in radical polymerization by ESR spectroscopy has been very difficult, mainly due to both the labile nature and the extremely low concentration of the propagating radicals. This problem was partly solved by the development of the TM110-mode cavity by Kamachi with a help of the JEOL research group. About 20 years ago, Kamachi et al. observed the ESR spectra of propagating methacrylate radicals under conditions similar to those in conventional polymerization by means of a specially designed flat cell and cavity called TM110-mode cavity [5]. The TM110-mode cavity has the same shape as a TE011-mode universal cavity turned sideways. The magnetic field of the irradiating microwave is normal to a horizontal plane, including the cavity axis, and the magnetic flux density in the TM110-mode cavity is lower than that with a TE011-mode cavity, if one uses a conventionally available cylindrical sample tube. Because a larger area is available for the ESR measurements under UV-light irradiation with the TM110-mode cavity, the wider lat cell is useful. ESR spectra were observed at an initiator concentration 1 or 2 orders of magnitude higher than the concentration usual radical polymerization using the TM110-mode cavity. Two important results bearing on the fundamentals of radical polymerizations were obtained through the development of the TM110-mode cavity. One was the observation of propagating radicals in real radical polymerization systems. The other was clear evidence for the presence of steady state radical concentrations during radical polymerizations. From the beginning of the 1990’s, relatively well resolved ESR spectra of propagating radicals have been observed using a commercially available TE011-mode universal cavity and normal sample cell, due to both improvement in ESR spectrometers and careful optimization of the preparation of the sample [5, 10-12].

Difficulty in direct detection of ESR spectra of propagating radicals is also due to a complexity of the radical polymerization reactions. It is well known that a radical polymerization reaction involves several elementary processes. Typical elementary processes are shown in Figure 3. In the figure species which have an unpaired electron of a radical.

![Fig.1 Structures of monomers and propagating radicals generated from corresponding monomers.](image1)

![Fig.2 ESR spectrum of propagating radicals of methyl methacrylate (MMA) along with its proposed structure.](image2)

![Fig.3 Elementary processes of radical polymerization. “I” is an initiator, “R” is a radical generated from the initiator, “M” is a monomer, “M_n” is a polymer with degree of polymerization of n, and “H-X” is a compound with a hydrogen that easy to abstract. “k” is a rate constant of each reaction. “•” represents an unpaired electron of a radical.](image3)
ESR observable, which means that various kinds of radical species coexist in the polymerization system. In principle, each species can be observed separately as model radicals with the aid of controlled radical polymerization methods as described in the latter part of this paper. However, direct detection of each of the radical species in Figure 3 one by one is very difficult or almost impossible. Especially, the conditions for detection of the propagating radicals during polymerization reactions and measurement of the ESR spectra should be optimized very carefully.

Radicals generated from azo-initiators.

The initiation process is a two steps reaction: the 1st step is decomposition of an initiator to form radicals and the 2nd step is an addition of the radical to a first monomer to form primary propagating radical as shown in Figure 3. The 1st step reaction can be observed by ESR in a separate procedure. The case of 2,2’-Azobis(2-methylpropionitrile) (AIBN) will be shown as an example. AIBN was decomposed by heating (to 60-80 °C) or upon irradiation to generate two copies of the same radical by cleavage of C-N bond and generating N₂ gas. This radical can be observed by ESR. The ESR spectrum of the radical is shown in Figure 4 along with its simulated spectrum. The primary feature of the spectrum is a relatively large heptet with small equivalent three line splitting due to presence of the nitrogen nuclei (I = 2/2). The values of coupling constants shown in the Figure 4 are reasonable for the structure and the simulated spectrum has features very close to the experimental spectrum.

Similarly, the ESR spectrum of initiating radicals generated from dimethyl 2,2’-azo-bis(2-methylpropionate) (MAIB) were able to be observed as shown in Figure 5. The spectrum displayed a relatively large heptet with small 1:3:3:1 four line splitting due to the methyl protons. Primary propagating radicals (RM•) will be formed by an addition of the radicals to a first monomer.

When an excess amount of monomer is added to the initiator solution, radical polymerization will proceed upon heating or irradiation in a sample cell. The propagating radicals formed in the solution can be observed by ESR.

Direct Detection of Propagating Radical during Radical Polymerization by ESR

Well-resolved ESR spectra of the radicals present in the polymerization of styrene and its derivatives, diene compounds, methacrylates, vinyl esters, and vinyl chloride were studied in benzene or toluene solution under usual polymerization conditions [5-7, 10-16]. Selected examples of ESR spectra of these propagating radicals observed during polymerization reactions are shown in Figure 6-13. They are well-resolved and show the characteristic features of hyperfine structures. Since values of hyperfine splitting constants were determined very precisely from these spectra, all of these spectra were reasonably well simulated as the corresponding propagating radicals, also shown in the Figure.

**tert-Butyl Methacrylate (tBMA)**

When a mixture of monomer and a radical initiator was heated or photo-irradiated in an ESR sample cell, propagating radicals were formed and the polymerization proceeded. Well-resolved spectra of the propagating radicals of tert-butyl methacrylate (tBMA) have been detected in such polymerization systems at various temperatures as shown in Figure 6. 16-line spectra were clearly observed. They were different from the ESR spectra previously reported for methacrylates (13-line or 9-line...
The β-methylene protons and the two stable conformations. The intensity of the inner 8 lines increased with increasing temperature, indicating that there are two exchangeable conformations whose existence have been shown in the elucidation of ESR spectra of methacrylates [5]. 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 βBMA at 150 °C is shown in Figure 7 along with the simulated spectrum. The spectrum is accurately simulated using hyperfine splitting constants of 1.40 mT for one methyl 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 7.

**Methyl Methacrylate (MMA) 13-line and 16-line Spectra**

ESR spectra of the propagating radicals present in MMA radical polymerizations are shown in Figure 8. A 13-line ESR spectrum has been observed for the propagating radicals in MMA polymerization using TM110-mode cavity. Figure 8a shows an ESR spectrum of the propagating radicals of MMA in radical polymerization at low resolution. This is the so-called 13-line spectrum that has been observed for MMA polymerization systems. The resolution of the spectrum can be improved by choosing smaller values of modulation width and the resulting highly resolved ESR spectrum of the MMA propagating radicals is shown in Figure 8b. A small 1:3:3:1 quartet splitting due to methyl protons in methyl ester can be observed in the well resolved spectrum. The presence of small quartet splitting clearly indicates that the structure of the radical is the same as that we have estimated as shown in Figure 8. On the other hand, the interpretation of the spectrum turned out to be more complicated by an overlapping of the spectroscopic lines and lowering the S/N ratio due to the presence of the small quartet splitting.

Therefore deuterated MMA (MMA-d3) was used as a monomer in order to simplify the spectra by selective observation of only the α-methyl and β-methylene protons as in the case of βBMA. In MMA-d3 three methyl protons of the methyl ester are replaced by deuterium and since splitting due to deuterium nuclei is 1/6 smaller than that of hydrogen nuclei it is coalesced in the line width. Therefore, only the splitting due to α-methyl and β-methylene protons were observed in the spectra. The spectrum obtained during the polymerization of MMA-d3 is shown in Figure 8c. It is a 16-line spectrum that can be interpreted just like that of βBMA as discussed above.

Now, we can say that the 13-line and 16-line spectra are essentially the same spectrum. The detection of 16-line spectrum also indicates that the propagating MMA radical has a sufficiently long chain length for kinetics study, especially for estimation of k_p as discussed later.

**Styrene**

ESR spectra of the propagating styrene radicals were clearly observed in a bulk polymer-
ization at various temperatures under irradiation. A typical example of the ESR signal of a propagating styrene radical in a conventional radical polymerization is shown in Figure 9. Simulation of the spectrum provides a close fit with the observed spectrum of the styrene propagating radical; both low and high resolution spectra are shown. These spectra were observed with different modulation width under almost the same conditions. The concentration of the propagating radicals can be precisely estimated by the low resolution spectrum because it has better S/N ratio. Hyperfine splitting constants can be measured precisely using the high resolution spectrum.

1,3-Butadiene

A well-resolved ESR spectrum was observed in the radical polymerizations of the 1,3-buta
diene with BPO, although a higher concentra
tion of initiator than usually employed for a radical polymerization (5 mol% for monomer) was necessary to obtain a sufficiently resolved spectrum to allow investigation of the behavior of the propagating radical (Figure 10) [15]. Moreover, the steady state of the radical concentra
tion in the polymerization was con
cirmed by the time dependency of the intensity of the ESR signal at constant magnetic field during irradiation with light (Figure 11) [15]. The steady state radical concentration had been an assumption in a kinetics study of radical poly
erizations. Now, ESR provides experimental evidence for the steady state [5,10].

Vinyl Acetate

The ESR spectrum of propagating radicals observed during radical polymerization of vinyl acetate at 5 °C is shown in Figure 12 along with its simulated spectrum. Resolution of the experimental spectrum is much improved from that observed using a TM110-
mode cavity. The spectrum shows splitting due to one α-proton and two β-methylene protons. Values of these couplings can be precisely measured from the spectrum, although one by one critical assignment is impossible only from these values. Each line split by α- and β-protons exhibits further splitting due to not only methyl protons but also γ-proton because more than five splitting lines can be observed.

Vinyl Chloride

Measurements of ESR spectra of propagat
ing vinyl chloride radicals were performed by photo-initiated polymerizations with BPO in benzene solution [29]. The spectrum is reasonably assigned to be a normal vinyl chloride propagating radical with hyperfine coupling constants. As shown in Figure 13, clear equivalent quartet due to nuclear spin of the chlorine nuclei (I = 3/2; 35Cl) was observed. In principle, coupling of isotope of chlorine (37,39Cl) should be also considered. However, the spectrum was not sufficiently well-resolved to show the difference in the hyperfine splitting constants between the isotopes. The obtained signal was reasonably well simulated using the above hyperfine coupling constants, as shown in Figure 13. The hyperfine coupling constant of 1.85 mT due to α-proton is similar to that of the propagating radical of vinyl acetate, suggesting that the radical reactivity of the propagating radical is similar to that of vinyl acetate. To our knowledge, this is the first example of a detection of an ESR signal of propagating vinyl chloride radicals in solution. Careful choice of the conditions is very important to generate the simple, clear, and well-resolved signal.

Results and Outlook

Owing to both continuous development of ESR spectrometers and optimization of measure
tion conditions, various kinds of spectra for propagating radicals, which were previous
ly extremely difficult to observe, were recorded at high resolution. These spectra can pro
gide significant information on the nature of propagating radicals because they are obtained from actual polymerization systems. From the spectra shown in this paper, detailed structural information can be obtained from the values of the hyperfine splitting constants. Experimental evidence also determined that there is a steady state of radical concentration in the polymer
erizations. In formation on the dynamics of the terminal radicals can be obtained form the spectra obtained at various temperatures as shown in the case of ESR spectra of methacryl
te propagating radicals. Activation energies of the rotational motion of the terminal radical
can be estimated from the results allowing the structures, dynamics, and kinetics of the propagating radicals to be discussed based on these ESR spectra.

Combination of ESR and Controlled Radical Polymerization Methods

Combination of ESR and Controlled Radical Polymerization Methods

Generation of Model Radicals from Precursors Prepared by Controlled Radical Polymerization Methods

In the following two sections, two further examples of the application of ESR spectrosc
y to conventional radical polymeriza
tions based on information obtained from con
trolled/living radical polymerizations will be demonstrated. First is estimation of effect of chain length on propagating radicals which is elucidated by ESR conducted with the aid of polymers prepared by ATRP. Second, is detection of chain transfer reactions on propagating radicals during the polymerization of BA.
The advantage of ESR is that the value of $P_n \bullet$ in these equations can be determined from the observed ESR spectra of the 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. Therefore ESR was employed to examine and quantify some intermediates in an ATRP which should provide a deeper understanding of the ATRP process, including identification of the structure and concentration of the paramagnetic species involved in the polymerization [30-33]. Although it is very interesting, and important for investigation of ATRP, the structural features of the paramagnetic transition metal compounds will not be discussed in this paper.

Differentiation of the Chain Length of Propagating Methacrylate Radicals by ESR

The spectrum of a propagating methacrylate radical is completely simulated 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 3b. A characteristic point of this result is estimation of different hyperfine splitting constants 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 on the time scale of the ESR measurement. Thus, it leads to a 16-line spectrum (2 $\times$ 2 $\times$ 4). 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 [14-20]. When the carbon-halogen bonds are cleaved homolytically by reaction with organotin compounds, model radicals of propagating chains with given chain length can be generated (Fig. 15 below) [21].

**Differentiating Between Chain Lengths of Propagating Radicals of tBMA**

First, a dimeric model radical precursor was prepared by ATRP (Fig. 14 below). The spectrum of a propagating methacylate radical is completely simulated 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 3b. A characteristic point of this result is estimation of different hyperfine splitting constants 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 on the time scale of the ESR measurement. Thus, it leads to a 16-line spectrum (2 $\times$ 2 $\times$ 4). 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 [14-20]. When the carbon-halogen bonds are cleaved homolytically by reaction with organotin compounds, model radicals of propagating chains with given chain length can be generated (Fig. 15 below) [21].
prepared by ATRP and purified. A model dimeric 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 radical observed at 150 °C showed a 12-line spectrum, as shown in Figure 17. The two β-methylene protons are almost equivalent in small radicals at such a high temperature. This finding indicates that rotation of the radical chain end is too fast 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 resulting in a 16-line spectrum, model radical precursors with degrees of polymerization (Pn) of 30, 50, and 100 were prepared by ATRP. Polymers with calculated molecular weights and low polydispersity were obtained. ESR spectra of radicals generated from these precursors were observed at various temperatures. Although the lifetime of the model radicals are very short at 150 °C, clear and well-resolved spectra were observed. These spectra showed similar temperature dependence to that shown in Figure 6. In the case of Pn = 100, a 16-line spectrum was clearly observed at temperatures lower than 120 °C. 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 Pn = 50 and 30 where the intensity of the inner 8 lines seems to coalesce more clearly to a single line at 150 °C. The ESR spectra appears 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 12-line spectrum begin to separate into two lines at Pn = 30, and the separation becomes larger with increasing Pn owing to the lower rate of rotation. The separation was more clearly observed in the propagating radical, indicating that mobility of the chain end radical is restricted.

Comparison of the ESR spectra of dimeric model radical (Fig. 17), model radicals with Pn = 100, and radicals in polymerization systems (Fig. 7) at 150 °C are shown in one figure, Figure 18. A comparison of the separation of the inner lines indicates that Pn of the propagating radical is higher than 100. Values of hyperfine coupling constants measured from these spectra, were plotted against chain lengths. They seemed to show a nearly linear correlation between hyperfine coupling constants and chain lengths in the range up to Pn = 200. Molecular weight (Mn) of the isolated polymers from polymerization system was determined to be 30,000 (Pn = 210) by SEC. The interpretation of the ESR spectra suggests that they correspond to "long" propagating radicals, and are in agreement with SEC. Before these experimental results ESR spectra and overall SEC results did not correlate. However, more experimental results are needed for a comprehensive correlation of kinetic data with ESR spectra.

We can conclude that observation of a 16-line spectrum in ESR measurements can be ascribed to "polymeric" radicals with more than 100 monomer units. Similar differences in ESR spectra were observed for polyMMA radicals generated in situ (Fig. 8). Although the spectra are more complicated, with a small quartet due to ester methyl protons, the ESR spectrum of polyMMA recorded during a polymerization showed a basic 16-line spectrum and the dimeric model radical with a terminal MMA radical showed a 12-line spectrum. Therefore ESR spectroscopy has provided structural information on the propagating radicals at their chain ends.

Direct information on the chain length of the radicals from ESR measurements had not been
reported before and is reported here for the first time.

Further information on the dynamic behavior of the propagating radicals can be obtained from these ESR spectra. The temperature dependence of these spectra can be simulated by consideration of the dynamics of conformational changes of the radicals. The average exchange time between the two conformers was calculated from the simulation of the spectra. The activation energy for rotation of the terminal \( \text{C}_\alpha - \text{C}_\beta \) bond was estimated to be 21.2 kJ/mol [13].

**Clarification of the Mechanism of Chain Transfer Reactions in Radical Polymerizations of Acrylates**

**ESR Spectra Observed during the Polymerization of tert-Butyl Acrylate and Interpretation of the Spectra**

Interpretation of ESR spectra observed in acrylate radical polymerizations have been very difficult [34-40]. The ESR spectra observed during radical polymerization of acrylates are very different from those from methacrylates, even under almost identical conditions (Fig. 19). 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 (tBA) as shown in Figure 19. A 6-line spectrum or doublet of triplets with narrow line width was observed at -30 °C. This spectrum can be reasonably assigned to be a propagating radical with two \( \beta \)-methylene protons (1:2:1 triplet) and one \( \alpha \)-proton (1:1 doublet). However at 60 °C, a totally different 7-line spectrum with broader line width was observed. The latter spectrum was much easier to observe than the former one, but traces of the 6-line spectrum can be seen in the 60 °C spectrum. However, the amount of species giving rise to the spectrum is 1000 times smaller than the species that are the predominant source of the high temperature spectrum. At -10 °C, overlapped spectra of the first and latter spectrum were observed (Fig. 19). Signal intensity due to the species present in the higher temperature spectrum with broader line width increased with time. These results suggest that the species responsible for the spectrum observed at -30 °C converted to the species providing 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 have 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 the ESR spectra of model radicals with various chain lengths generated from polymeric radical precursors prepared by ATRP. This analysis helped to resolve the ambiguity.

Precursors of acrylate \( \text{P}_n^* \) with \( n = 15, 50, \) and 100 were prepared by ATRP. Polymers with calculated molecular weights and low polydispersities were obtained. The model radicals were generated by a reaction with organotin compounds and the radicals were observed by ESR spectroscopy [27]. The ESR spectrum observed for \( \text{P}_n^* = 100 \) are shown in Figure 20. The radicals provided almost the same 6-line (doublet of triplets) ESR spectra of propagating radicals present at low temperature (-30 °C) as shown in Figure 19. The observed 6-line spectra changed after raising the temperature to 60 °C, and the change in the spectrum is in agreement with the ESR spectra observed directly during the radical polymerization. The model systems do not contain any monomer and the spectroscopic change occurred without propagation. This suggests
that a chemical reaction is responsible for the observed changes. The chemical reaction maybe a chain transfer reaction from the initial formed terminal radicals to form mid-chain radicals as discussed earlier for radical polymerizations of acrylates.

One additional piece of evidence supporting the formation of a mid-chain radical was obtained from an examination of hydrogen abstraction from polyacrylates. This mid-chain radical can be formed by hydrogen abstraction from polycarbonylates by oxygen centered radicals. PolyBA and tert-butyl peroxide (tBPO) were dissolved in benzene, under irradiation the mixture gave the ESR spectra shown in Figure 21. The spectrum was very similar to that of the 1,5-hydrogen shift reaction. It is known that polyacrylates prepared by conventional radical polymerization procedure have many branches [41, 42]. An ESR study has now provided direct evidence for the origin of the branching. It should also be noted that an estimate of \( k_p \) for acrylates is difficult by ESR which would provide the sum of the concentration of the much more active growing terminal radicals and less active mid-chain radicals.

Clarification of Mechanism of Radical Migration using Uniform Oligomeric Model Radicals

Since changes from low temperature spectrum to the one at higher temperature were clearly observed, even in model radical systems with fixed chain lengths, the possibility of chemical transformation remained. The ambiguity was solved by ESR spectroscopy of several purified oligomeric radical precursors prepared by ATRP. GPC elution diagrams of model radical precursors of dimer, trimer, tetramer, and pentamer are shown in Figure 25 along with the GPC of a mixture of the oligomers. As shown in the figure, separation and purification of the oligomers were successful. Model radicals with clearly defined structures were generated by the reaction of the corresponding allyl bromides (H-ethyl acrylate (EA)-tBA-Br, H-EA-tBA-tBA-Br, H-EA-tBA-tBA-Br, H-EA-Br, H-EA-tBA-tBA-tBA-Br) with an organotin compound under irradiation. The resulting radicals had structures of hydrogenated radicals, i.e., H-EA-tBA, H-EA-tBA-tBA, H-EA-tBA-tBA-tBA, and H-EA-tBA-tBA-tBA-tBA, respectively. Each of these radicals was investigated by ESR spectroscopy at various temperatures. Clear well-resolved spectra were observed and precise values for hyperfine coupling constants were determined from the spectra. The ESR spectrum of the dimeric radical (H-EA-tBA-) showed a doublet of triplets in each spectrum taken at various temperatures within the range of -30 to +150 °C. The doublet and triplet can reasonably be considered to be due to the splitting from the \( \alpha \)-proton and two equivalent \( \beta \)-methylene protons, respectively. Nothing happened to the dimeric radical even at higher temperatures (Fig. 26). On the other hand, model trimeric and tetrameric radicals showed a clear temperature dependent irreversible change, as discussed below.

In the case of the model trimeric radical (H-EA-tBA-tBA+), the spectrum observed at -30 °C (Fig. 27) was very similar to that of the dimeric radical. This spectrum is assigned to a chain end radical as shown in the figure. ESR spectra were measured every 30 degrees 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. From 0 °C to 60 °C, the observed spectra were attributable to two kinds of overlapping spectra. The change was complete at 120 °C. The resulting spectrum, observed at higher temperatures, was totally different from that at lower temperatures (Fig. 27). 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 27. The spectrum can be simulated using the hyperfine splitting constants shown in the figure. The most important feature of this simulation is a small triplet that appeared 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.

A similar ESR study was done for the tetrameric model radical (H-EA-BA-BA-BA•). The ESR spectra at -30 °C and 120 °C are shown in Figure 28. The low temperature spectrum, observed at -30 °C, was very similar to those from the dimeric and trimeric model radicals. A similar irreversible spectroscopic change took place, as in the case of the trimeric model radical, at higher temperatures. 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 ethyl unit, which is located two units before the other end unit, through a six-membered ring structure (Fig. 28). The transferred radical should have mid-chain type structure with methylene groups at both sides (H-EA-BA(A•)-BA-BA-H). The spectrum of the radical at 120 °C shown in Figure 28 is ascribable 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.

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 the chain transfer reaction in an acrylate radical polymerization is a 1,5-hydrogen shift that occurs through a six-membered ring structure. Formation of a six-membered ring is a kinetically favored process and the transfer occurred from a secondary radical to form a thermodynamically more stable tertiary radical. One further piece of information can be obtained from the result of the pentamer since the pentamer provides one more chance to migrate from a mid-chain radical to the other chain end. However, this migration was not observed for the pentameric model radical which has H-EA-BA-BA-BA-BA• structure. 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.

**Summary and Perspective**

When the ESR spectra obtained by direct detection in a radical polymerization processes are compared with those of model radicals generated from well defined radical precursors prepared by ATRP, it is easier to understand what happens at each step of the elementary processes involved in radical polymerizations. This information help define the reaction mechanisms, which otherwise have been speculated upon without direct experimental evidence. ESR spectroscopy has provided unambiguous proof of the process for several reactions involved in radical polymerization with...
the aid of materials prepared by controlled radical polymerization techniques. In general this approach can be applied to any chemical reaction, not only to a radical reaction, which has well-defined starting materials and final products but ambiguous intermediate products.

Research using uniform oligomeric model radicals provides the possibility for expansion of the research field. In general, precise quantum chemical calculations are difficult to apply for polymeric radicals with long chain lengths but theoretical calculations can be conducted for such small radicals. The small radicals can provide highly resolved ESR spectra and they can provide precise values of hyperfine splitting constants. Polymeric radicals usually show larger line width making the precise determination of the splitting constants more difficult. The values are strongly related to electronic nature of the radicals and can be evaluated by the results of the calculations. ESR itself is a quantum mechanical phenomenon. The combination of ESR, ATRP, and theoretical calculations lead the way to study of a deeper connection between experimental results and theoretical calculations.

It was also important to examine and quantify some intermediates in ATRP, to provide a deeper understanding of the ATRP process, including identification of the structure and concentration of the paramagnetic species involved in the process [14, 30, 43-48]. Although it is very interesting and important for investigation of ATRP, the structural features of the paramagnetic transition metal compounds will not be discussed in this paper.

**Experimental**

Monomers, initiators, copper salts, and ligands were purified in the usual manner. Presence of boron-citriate terminal groups and chain lengths of the radical precursors were checked by measurements of Electron Spray Ionization (ESI) mass spectra. Generation of model radicals from precursors was conducted by a reaction with an organotin compound under irradiation. ESR spectra of radicals were recorded on a JEOL JES RE-2X spectrometer operating in the X-band, utilizing a 100 kHz field modulation, and a microwave power of 1 mW. A TE011 mode universal cavity was used. Measurement temperature was controlled by JOEL DVT2 variable-temperature accessory. ESR measurements were mainly performed in mesitylene at 150 and 120 °C and in toluene at 90, 60, 30, and -30 °C. Spectroscopic simulations were carried out by JEOL IPRIT Data Analysis System. Molecular weights and molecular weight distributions were roughly estimated using a TOSOH CCP&8020 series GPC (SEC) system with TSK-gel columns. Polystyrene standards were used to calibrate the columns.

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