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A combination of Electron Spin Resonance spectroscopy/atom transfer radical polymerization (ESR/ATRP) techniques for fundamental investigation of radical polymerizations of (meth)acrylates

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Dedicated to Professor Krzysztof Matyjaszewski on the occasion of his 65th Birthday.

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A B S T R A C T

This paper results from combining Electron Spin Resonance (ESR) spectroscopy and atom transfer radical polymerization (ATRP) to study the basic chemistry of radical polymerizations. This combination of analytical and controlled preparation techniques can provide information on chain length of propagating radicals and chain transfer reactions to polymers which has been previously difficult or impossible to study by direct detection of radicals in radical polymerizations by ESR.

Two results are obtained by the ESR/ATRP combination technique. The first provides an estimation of the effect of chain length on the structure of methacrylate propagating radicals, especially in the initial stage of radical polymerizations. Model radical precursors of dimeric, trimeric, tetrameric, and pentameric structures of *t*BMA and MMA were prepared by ATRP. The corresponding model radicals were generated from these precursors and were observed by ESR at various temperatures. The ESR spectra provided direct information on chain length dependent changes of the averaged structures at the chain ends of the model propagating radicals, indicating that distortion in dihedral angles between chain end pπ-orbital and C_β-H bonds increased with increasing chain length.

The second result provides information on the radical migration reactions during the polymerization of acrylates. Radical precursors of ethyl-, *n*-butyl-, and dodecyl acrylates with various chain lengths ($DP = 10$, 25, 60, etc.) were prepared by ATRP. Model propagating radicals were generated from these precursors and were observed by ESR at various temperatures. These radicals showed chain length dependent spectroscopic change due to radical migration reactions from model propagating to mid-chain radicals with increasing temperature. Longer chained radicals with the same ester side groups showed easier formation of mid-chain radicals. An examination of side group dependency indicated that, longer alkyl side groups showed easier radical migration reactions. The development of ATRP enabled us to resolve these problems associated with side reactions in radical polymerizations.

1. Introduction

Electron spin resonance (ESR) spectroscopy is the most powerful instrument for investigation of the nature of the radical species in radical polymerizations. When well-resolved spectra can be observed, the spectra provide information not only on the structures, properties, and concentration of radicals but also information on the initiating and propagating (oligomeric and polymeric) radicals [1–12]. However, 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 in the polymerization medium. Beginning in the early 1990's, relatively well resolved ESR spectra of propagating radicals have been observed using a commercially available cavity and normal sample cell, due to both improvement in ESR spectrometers and careful optimization of the preparation of the sample [5,13–19]. Well-resolved spectra provide detailed information on the structure and chemical properties of the radicals. 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. Based on these spectra, kinetic analysis, especially for estimation of propagating rate constants (k_p) of the monomers, was

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performed [15–19] and ESR spectroscopy was successfully applied to quantify radical concentrations in the polymerizations.

Atom transfer radical polymerization (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 [20–26]. The polymers formed in an ATRP contain terminal carbon-halogen bonds. This characteristic structure of the polymers resulting from synthesis by ATRP provides new opportunities for ESR to study the fundamentals of radical polymerization chemistry in detail. Specifically, since Giese et al. reported that these carbon-halogen bonds can be homolytically cleaved by reaction with organotin compounds [27], this allows various radicals that model the transient active species in radical polymerizations 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.

When conducting ESR spectroscopy on radical polymerizations, direct detection in a conventional polymerization and this new method using model radicals based on controlled radical polymerization technique complement each other. When the ESR spectra obtained by direct detection in a radical polymerization processes (Fig. 1a) are compared with those of model radicals generated from well-defined radical precursors prepared by ATRP (Fig. 1b), it is easier to understand what happens at each step of the elementary processes in radical polymerizations. This information will help define the reaction mechanisms, which otherwise have been speculated upon without direct experimental evidence. In general, any chemical reaction, not only radical reactions, has well-defined starting materials and final products but ambiguous intermediate products. ESR spectroscopy has provided unambiguous proof of the process for several reactions involved in radical polymerization with the aid of controlled radical polymerization technique.

Thus the combination method of ATRP and ESR has brought improvements to the procedures available for the basic study of the chemistry of radical polymerizations and contributing reactions. For example, polymeric *tert*-butyl methacrylates (*t*BMA) with various chain lengths had been prepared by ATRP and model radicals with corresponding structures were generated from the polymers and were observed by ESR [28]. The ESR spectra clearly showed a chain length dependent change, and interpretation of these spectra clarified that the ESR spectrum observed during actual polymerization systems was due to polymeric radicals longer than DP = 200 [28]. Acrylate model radicals were also investigated. ATRA and ATRP provided dimeric, trimeric, tetrameric, and pentameric model radical precursors and corresponding model radicals were generated and were observed by ESR. The ESR spectra of these model propagating radicals at various temperatures clearly showed that the chain transfer reaction during radical polymerizations of acrylates occurs through an intramolecular back biting reaction via 1,5-hydrogen shift mechanism through a formation of a six-membered ring structure [29–34]. Chain transfer reactions during acrylate radical polymerizations have been considered for more than 50 years and intramolecular 1,5-hydrogen shift mechanism was also proposed. The ESR/ATRP combination technique provided definite experimental evidences to enhance the fundamental research of radical polymerizations and reactions [29–34]. On the other hand, many unsolved problems in basic chemistry of radical polymerizations still remain.

In this paper, the application of ESR spectroscopy to clarify the fundamentals conventional radical polymerizations based on controlled/living radical polymerizations will be demonstrated through analysis of the results of two experimental procedures. First is estimation of effect of chain length on methacrylate propagating radicals especially in the initial stage of radical polymerizations by ESR conducted with the aid of precursors prepared by ATRP. In the initial steps of a polymerization, chain initiating radicals add the next monomer to sequentially form trimeric, tetrameric, and pentameric propagating radicals. The addition rate constants to form the oligomeric propagating radicals decrease dramatically with increasing chain lengths. Identification of changes in the structure and molecular dynamics of the radicals during such a dramatic change should be interesting. A systematic

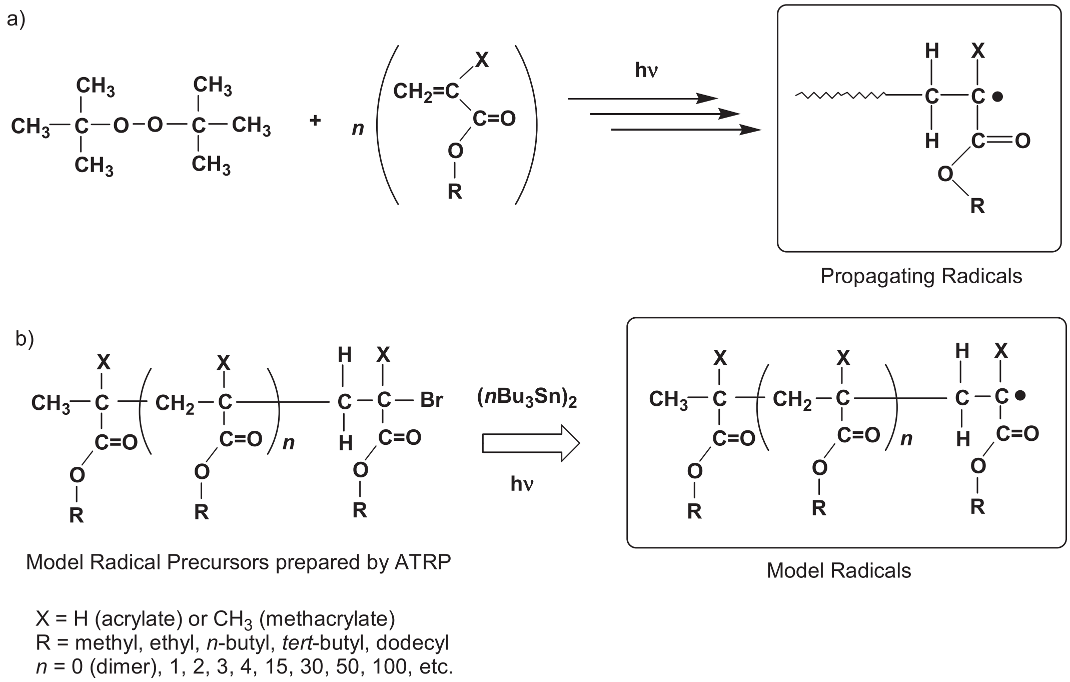

Fig. 1. (a) Generation of propagating radicals and (b) oligomeric model radicals. ESR spectra of methacrylates showed a chain length dependence. ESR spectra of acrylate radicals show clear proof of a 1,5-hydrogen shift.