Origin of 16-Line Spectra Observed in ESR Study of Radical Polymerization of *tert*-Butyl Methacrylate: Clear Evidence for ESR Detection of Polymeric Propagating Radicals

Atsushi Kajiwara,* Kumiyo Maeda, and Noritaka Kubo

Nara University of Education, Takabatake-cho, Nara 630-8528, Japan

Mikiharu Kamachi*

Fukui University of Technology, 3-6-1, Gakuen Fukui 910-8505, Japan

Received July 26, 2002

ESR (electron spin resonance) spectroscopy can theoretically provide direct information on the structures, properties, and concentrations of propagating radicals.[1,2] Accordingly, ESR spectroscopy is a promising technique for obtaining information on the propagating radicals in the radical polymerization, if well-resolved ESR spectra of propagating radicals are observed.[2−4]

We have detected highly well-resolved ESR spectra in the radical polymerizations of styrene and its derivatives, diene compounds, methacrylates, and vinyl esters in benzene or toluene.[3−10] All these spectra are reasonably simulated as propagating radicals. In the extension of ESR studies on the radical polymerization, we measured ESR spectra of propagating radicals of *tert*-butyl methacrylate (*t*BMA) at various temperatures. In the course of the measurement, 16-line spectra instead of 13-line spectra, which were detected so far in ESR spectra of methacrylates,[2,3] were clearly observed in the range 30−150 °C. The 16-line spectrum was previously observed in the flow method using methacrylic acid,[1b] but we have never seen the 16-line spectra of the propagating radicals in ESR study on the radical polymerizations of methacrylates so far. Judging from the observation in the flow method, the 16-line spectrum might be ascribed to oligomeric radicals. There has been no clear information on chain length of the ESR-detected propagating radicals. So, we investigated the origin of the 16-line spectra observed in the polymerization of *t*BMA. In this communication, we show that the 16-line spectra are due to polymeric radicals, and in addition, we would like to provide quite important information on the dynamic behavior of the propagating radicals.

We prepared model radical precursors by atom transfer radical polymerization (ATRP) reported by Matyjaszewski et al.[11−16] ATRP can provide polymers with controlled molecular weights, and the resulting polymers have terminal carbon−halogen bonds. Polymers with narrow molecular weight distribution (M_w/M_n = 1.14−1.21) were prepared by this method. Polymeric and oligomeric model radicals were formed from the corresponding precursors by the reaction with organotin compounds reported by Giese et al.[17] The radical formation reactions were performed in ESR tube under irradiation at various temperatures.[18]

ESR spectra observed in the polymerization of *t*BMA at various temperatures are shown in Figure 1. The

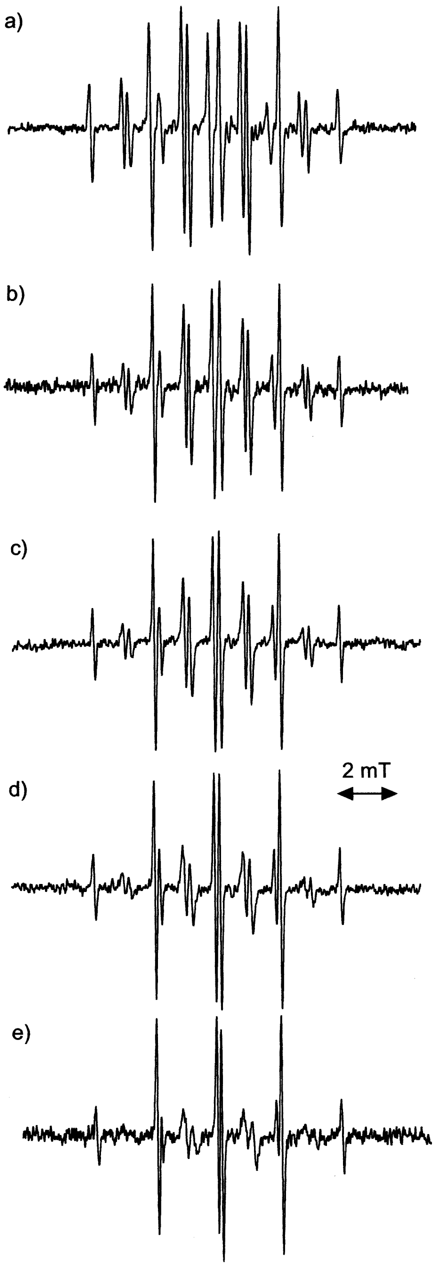

Figure 1. ESR spectra of propagating radicals of *t*BMA at various temperatures: (a) 150, (b) 120, (c) 90, (d) 60, and (e) 30 °C.

intensity of the inner eight lines decreased with lowering the temperature, indicating that there are two exchangeable conformations whose existence has been shown in the elucidation of ESR spectra of methacrylates so far.[2] To confirm the presence of two conformations, we measured ESR spectra at 150 °C, indicating that the inner eight lines increased furthermore. The observed spectrum is completely simulated using hyperfine splitting constants which are 1.40 mT for one proton, 1.16 mT for one proton, and 2.17 mT for three protons (Figure 2). The hyperfine splitting constants of the two methylene protons are different, indicating that the spectrum is assigned to an averaged single conformation due to rapid exchange between the two conformations. The observation of nonequivalent methylene

---

* Corresponding author: phone +81-742-27-9192, Fax +81-742-27-9192, e-mail kajiwara@nara-edu.ac.jp.

10.1021/ma021205q CCC: $25.00

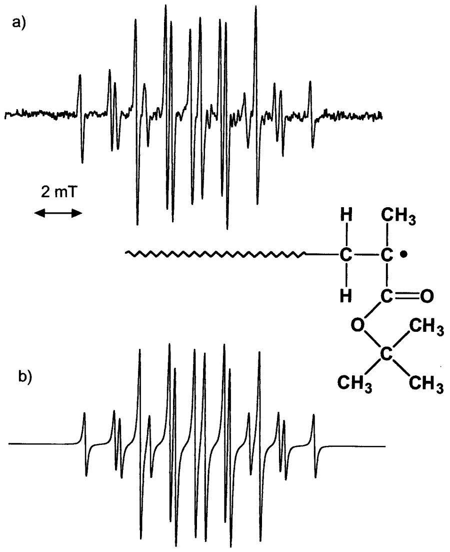

Figure 2. Structure of propagating radical of *t*BMA and ESR spectra of the propagating radical of *t*BMA at 150 °C (a) and its simulation (b).

protons means that the rate of the rotation of the end radical is not so fast as to be detected as equivalent methylene protons in the time scale of detection of ESR measurement.

ESR spectra of radicals from polymeric precursors showed a similar temperature dependence. Selected ESR spectra of these radicals with their degrees of polymerization of 100, 50, and 30 at 150 and 90 °C are shown in parts a, b, and c of Figure 3, respectively. In the case of $P_n = 100$, the 16-line spectrum was clearly observed at 90 °C (Figure 3a2). The intensity of the inner eight lines increased with increasing temperatures and seems to coalesce to a single line at 150 °C (Figure 3a1).

Similar ESR spectra were observed in radicals from polymeric precursors with $P_n = 50$. The intensity of the inner eight lines seems to coalesce more clearly to a single line at 150 °C (Figure 3b1). In the case of $P_n = 30$, the 16-line spectrum was observed at 90 °C (Figure 3c2). The inner eight lines coalesce more clearly to a single line at 150 °C (Figure 3c1). The ESR spectrum seems to be a 12-line spectrum, but the four lines coalesced insufficiently, indicating that the rate of the rotation of the end radical is not so fast as to be detected as equivalent methylene protons on the time scale of detection of the ESR measurement.

Oligomers with $P_n = 2-7$ were prepared, and ESR spectra of radicals generated from them were measured at 150 °C. The 12-line spectrum was clearly observed as shown in Figure 4a. The 12-line spectrum is simulated using hyperfine splitting constants, which are 1.23 mT for two protons and 2.17 mT for three protons (Figure 4b), and is easily assigned to a single radical that has two equivalent methylene protons and three methyl protons. Two equivalent methylene protons in the oligomer show clearly that free rotation of radical end is too fast to be detected as different methylene protons on a time scale of ESR spectroscopy. We can conclude that the inner four lines of the 12-line spectrum begin to separate two lines at $P_n = 30$ and that the separation becomes larger with increasing the degree of polymerization, 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 end radical is restricted.

Comparison of the ESR spectra of radicals with various chain lengths at 150 °C is shown in Figure 5. From the comparison of the separation of inner lines, the degree of polymerization of the propagating radical is higher than 100. This speculation was clearly confirmed by molecular weight (M_n) of the isolated polymer, which was determined to be 30 000 ($P_n = 210$) by GPC.

We can conclude that the origin of the 16-line spectrum in our ESR measurement is ascribable to polymeric radicals. ESR spectroscopy has provided structural information on the propagating radicals at chain end. Direct information on the chain length of the radicals has not been obtained before from ESR measurements. Data shown in this communication provide the information.

Further information on dynamic behavior of the propagating radicals can be obtained from these ESR spectra. The temperature dependence of these spectra can be simulated in consideration with dynamics of the

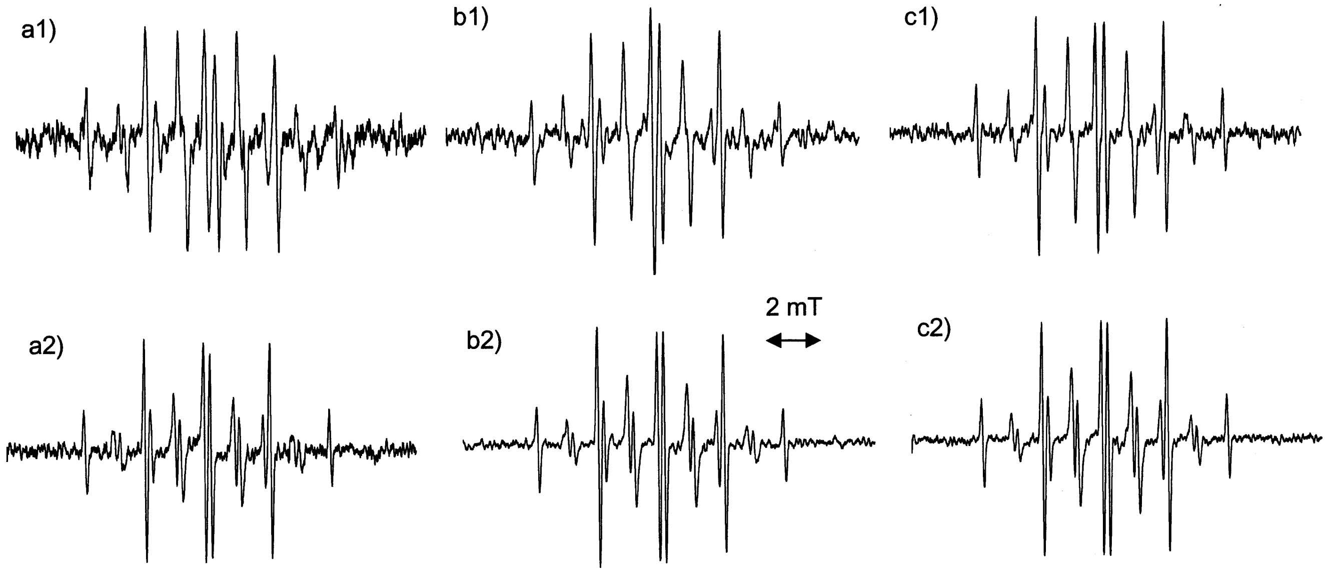

Figure 3. ESR spectra of model radicals of poly(*t*BMA) with given chain lengths: (a) $P_n = 100$, (b) $P_n = 50$, and (c) $P_n = 30$; (1) 150 and (2) 90 °C.

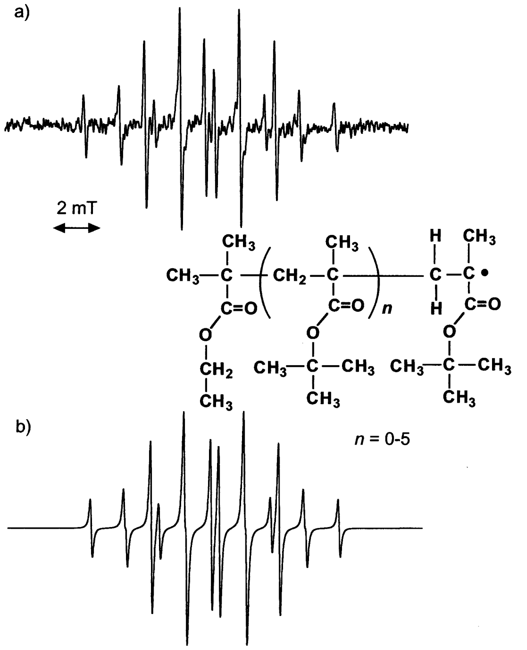

Figure 4. Structure of oligomeric model radical and ESR spectra of the oligomeric model radicals of *t*BMA ($P_n = 2-7$) at 150 °C (a) and its simulation (b).

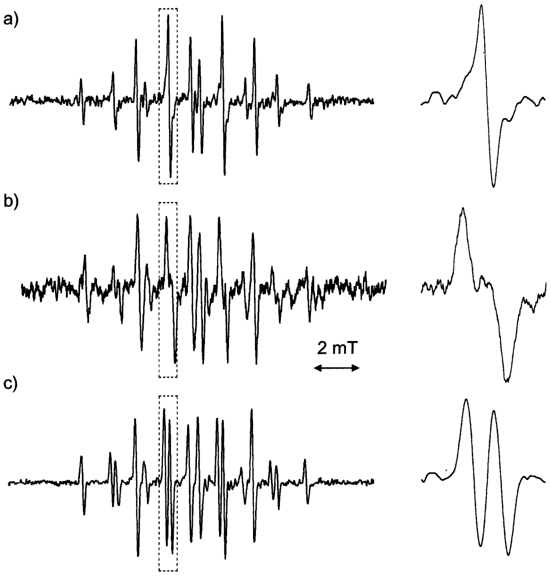

Figure 5. Comparison of ESR spectra of radicals with various chain lengths at 150 °C: (a) oligomeric model radical, (b) model radical with $P_n = 100$ and radicals in a radical polymerization (propagating radical). Characteristic lines (in dashed squares) were enlarged on the right-hand side.

Table 1. Averaged Exchange Time between Two Conformations in *t*BMA Propagating Radicals

temperature, °C	exchange time, ns
150	0
120	9.6
90	16.9
60	31.0

radicals.[19] The averaged exchange time between the two conformers was calculated from the simulation of the spectra in Figure 1 as shown in Table 1. The activation energy of a rotation of the terminal $C_\alpha-C_\beta$ bond was estimated to be 21.2 kJ/mol.[20]

Acknowledgment. The authors are grateful to Professor Krzysztof Matyjaszewski, Carnegie-Mellon University, for his kind advice for preparation of radical precursors by the ATRP technique. The authors thank Professor Antal Rockenbauer, Hungarian Academy of Sciences, for his kind permission to use his simulation program in consideration with dynamics behavior. Thanks are due to Professor Norikazu Ueyama, Dr. Taka-aki Okamura, and Mr. Hiroshi Adachi, Graduate School of Science, Osaka University, for measurements of ESI mass spectra of radical precursors. This research work was partly supported by Grant-in-Aid (No. 13650937) from Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References and Notes

(1) (a) Fischer, H. *Z. Naturforsch.* **1964**, *19A*, 267, 866. (b) Fischer, H. In *Polymer Spectroscopy;* Hummel, D. O., Ed.; Springer-Verlag: Berlin, 1974; pp 289−354.
(2) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.
(3) Kamachi, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 269.
(4) Kamachi, M.; Kajiwara, A. *Macromol. Symp.* **2002**, *179*, 53.
(5) Kamachi, M.; Kajiwara, A. *Macromolecules* **1996**, *29*, 2378.
(6) Kamachi, M.; Kajiwara, A. *Macromol. Chem. Phys.* **1997**, *198*, 787.
(7) Kamachi, M. In *Controlled Radical Polymerization*; ACS Symposium Series 685; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998; Chapter 9, pp 145−168.
(8) Kajiwara, A.; Matyjaszewski, K.; Kamachi, M. In *Controlled Radical Polymerization*; ACS Symposium Series 768; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2000; Chapter 5, pp 68−81.
(9) Kamachi, M.; Kajiwara, A. *Macromol. Chem. Phys.* **2000**, *201*, 2165.
(10) Kajiwara, A.; Kamachi, M. *Macromol. Chem. Phys.* **2000**, *201*, 2160.
(11) Wan, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(12) Wan, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(13) Kajiwara, A.; Matyjaszewski, K.; Kamachi, M. *Macromolecules* **1998**, *31*, 5695.
(14) Kajiwara, A.; Matyjaszewski, K. *Polym. J.* **1999**, *31*, 70.
(15) *Controlled Radical Polymerization;* ACS Symposium Series 685; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 1998.
(16) *Controlled Radical Polymerization*; ACS Symposium Series 768; Matyjaszewski, K., Ed.; American Chemical Society: Washington, DC, 2000.
(17) Giese, B.; Damm, W.; Wetterich, F.; Zeitz, H.-G. *Tetrahedron Lett.* **1992**, *33*, 1863.
(18) Monomers, initiators, copper salts, and ligands were purified in the usual manner. The presence of carbon−bromine terminal and chain lengths of the radical precursors were checked by measurements of ESI mass spectra. 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 TE_{011} mode cavity was used. The temperature was controlled by a JEOL DVT2 variable-temperature accessory. ESR measurements were performed in mesitylene at 150 and 120 °C and in toluene at 90, 60, and 30 °C. Spectroscopic simulations were carried out by a JEOL ESPRIT330 Data Analysis System. Molecular weights and molecular weight distributions were roughly estimated using a TOSOH CCP&8020 series GPC system with TSK gel columns. Polystyrene standards were used to calibrate the columns.
(19) Rockenbauer, A. *Mol. Phys. Rep.* **1999**, *26*, 117.
(20) Kajiwara, A.; Kamachi, M.; Rockenbauer, A., to be published.

MA021205Q