Temperature gradient interaction chromatography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis of air terminated polystyryllithium

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Abstract

The reaction products of polystyryllithium with air were characterized by size-exclusion chromatography, temperature gradient interaction chromatography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Polystyryllithium was prepared by anionic polymerization of styrene initiated with *sec*-butyllithium in cyclohexane under an Ar atmosphere. It was confirmed that polystyryl ketone, polystyryl alcohol, and directly coupled polystyrene were the major products in addition to the normally terminated polystyrene, which is consistent with the results in the literature. We could also identify the presence of methoxy and carboxylic acid end capped polystyrenes as well as dipolystyryl ether as minor products. Among the minor products, dipolystyryl ether has not been reported yet. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Living anionic polymerization has been used for a long time to make many useful polymers with a predictable molecular mass and a narrow molecular mass distribution. The living anionic polymerization technique needs to proceed under inert condition, either high vacuum or inert gas atmosphere, to keep growing polymer anions from undesired termination or other side reactions [1]. At the completion of chain growth, the anion chain ends can be utilized for various controlled reactions to yield end-functional polymers, block copolymers, branched polymers, and so on [2–6].

There have also been efforts to investigate in detail the reactions of anionic chain ends. For example, the reaction products from the treatment of polystyryl anions with oxygen or carbon dioxide have been characterized [7–10]. The reaction of polystyryllithium with oxygen is known to yield polystyryl alcohol, polystyryl ketone and directly coupled polystyrene in addition to the normally terminated polystyrene by proton transfer [8]. Aldissi et al. investigated the reaction of living oligoethylene anions with oxygen using mass spectrometry coupled with gas chromatography [11]. They also found

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hydroxy terminated oligoethylene and the coupled products as well as the normally terminated oligomers by proton transfer. These products from the reaction with oxygen could be explained by a radical mechanism via the formation of peroxides and alkyl/alkoxy radicals [11].

There exist more extensive studies on the reaction of polymer anions with carbon dioxide. Wyman et al. reported the formation of three different products, polystyrene carboxylic acid, dipolystyryl ketone, and tripolystyryl carbinol in addition to the normally terminated polystyrene [7]. Mansson [8] and Quirk et al. [10] confirmed the results but the relative yield of the products depended on the reaction condition such as the reaction medium controlling the association of the anion ends.

These studies employed size-exclusion chromatography (SEC) to separate the reaction products according to molecular mass and/or high-performance liquid chromatography (HPLC) or thin-layer chromatography to separate them by the functional group difference. In the past few years, we have shown that temperature gradient interaction chromatography (TGIC) can be used for both purposes. TGIC is a form of HPLC, in which the column temperature is varied in a programmed manner to control the retention of polymers during isocratic elution [12]. TGIC could fractionate polymers with high resolution in terms of their molecular mass [13–15], chemical heterogeneity [16–18] and the chain architecture [18–20].

Another emerging analytical technique, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has become a powerful tool to characterize the molecular structure of polymers. MALDI-TOF-MS employs a soft ionization method and is able to provide absolute molecular mass, composition, and functionality of intact polymers [21–27].

In this paper, we report the characterization results of the reaction products of polystyryllithium with air. Air is certainly not a well-defined chemical but it is well known that the air termination of polymer anions can induce the formation of various side products [28]. The main purpose of this study is to rigorously characterize the complex polymer mixtures by combining TGIC and MALDI-TOF-MS methods.

2. Experimental

2.1. TGIC

The TGIC apparatus consists of a solvent delivery pump (Polymer Labs LC 1150), a six-port sample injector (Rheodyne, 7125) equipped with a 100 μl injection loop, and a variable-wavelength UV–Vis absorption detector (TSP, Spectra 100) as a concentration detector. For the normal-phase TGIC (NP-TGIC) experiments, a bare silica (Nucleosil, 100 Å pore, 250×4.6 mm I.D.) and a mixture of light petroleum–CH_2Cl_2 (41:59, v/v) were used as stationary and mobile phases, respectively. The temperature of the separation column was controlled by circulating fluid from a programmable bath/circulator (Neslab, RTE-111) through a laboratory-made column jacket. The reversed-phase TGIC (RP-TGIC) system is essentially the same as the NP-TGIC system except for the column (Alltech, Platinum EPS, C_{18}, 100 Å, 53×7.0 mm I.D.) and the mobile phase (CH_2Cl_2–CH_3CN, 57:43, v/v). HPLC-grade CH_3CN, CH_2Cl_2 and light petroleum were purchased from Aldrich and filtered through a 0.2 μm membrane filter (Bio-Rad) before use.

For the SEC analysis, two mixed bed columns (Polymer Labs PL-mixed C, 300×8.0 mm I.D.) were used. Tetrahydrofuran (THF, HPLC grade, Aldrich) was the eluent and the column temperature was kept at 35 °C in a column oven (Eppendorf, TC-50).

2.2. MALDI-TOF-MS

For the MALDI-TOF-MS experiments, a Bruker Reflex III mass spectrometer was used. The spectrometer is equipped with a nitrogen laser (wavelength 337 nm), a pulsed ion extraction, and a reflector. Ions below $m/z = 400$ were removed by pulsed deflection. This instrument operated at an accelerating potential of 20 kV in the reflector mode. Polymer solutions (concentration lower than 2 g/l), a matrix [1,8-dihydroxy-9(10H)-anthracene, dithranol, Aldrich] solution (10 g/l), and a salt solution (silver trifluoroacetate, 1 g/l) were prepared in THF. A 5 μl volume of the polymer solution was mixed with 25 μl of the matrix solution and 1 μl of the silver trifluoroacetate solution, and 0.5 μl of the mixture

was deposited onto a sample target plate and allowed to dry in air at room temperature.

2.3. Materials

Polystyryllithium was prepared by anionic polymerization under an Ar atmosphere using *sec*-butyllithium and cyclohexane as the initiator and the solvent, respectively. The polymerization temperature was 45 °C. After all the monomer was consumed the reaction vessel was opened to the air. The orange color of the polystyryl anions disappeared in about 5 min. If air was bubbled into the reaction mixture, the color disappeared instantaneously. Air bubbling decreased the formation of the coupled polystyrenes, but the species in the products were identified the same.

3. Results and discussion

In Fig. 1A a SEC chromatogram of the polystyrene made from the air termination of the polystyryllithium is displayed. The elution peak consists of a low-molecular-mass major peak (i) and a high-molecular-mass shoulder (ii). The molecular mass of the major peak is consistent with the target molecular mass calculated from the feed ratio of the monomer to initiator, 4.4 kg/mol, while the molecular mass of the shoulder is two times as large as the major peak. The side product of twice the molecular mass is often found in polymers prepared by anionic polymerization and the major cause is known as oxygen mediated radical coupling of the polymer anions [28]. Fig. 1B displays an RP-TGIC chromatogram of the same polymer as shown in Fig. 1A. It clearly shows that RP-TGIC separates the polymers with higher resolution than SEC in terms of molecular mass. However, neither SEC nor RP-TGIC could separate them in terms of functionality.

On the other hand, the MALDI-TOF-MS analysis of the air terminated polystyrene shows that the polymer contains many different species as displayed in Fig. 2. The mass spectrum consists of a major envelope of peaks centered around $m/z=4500$ and a minor envelope around $m/z=9000$. In the magnified spectrum in Fig. 3A the major envelope actually consists of four different series of peaks. The m/z
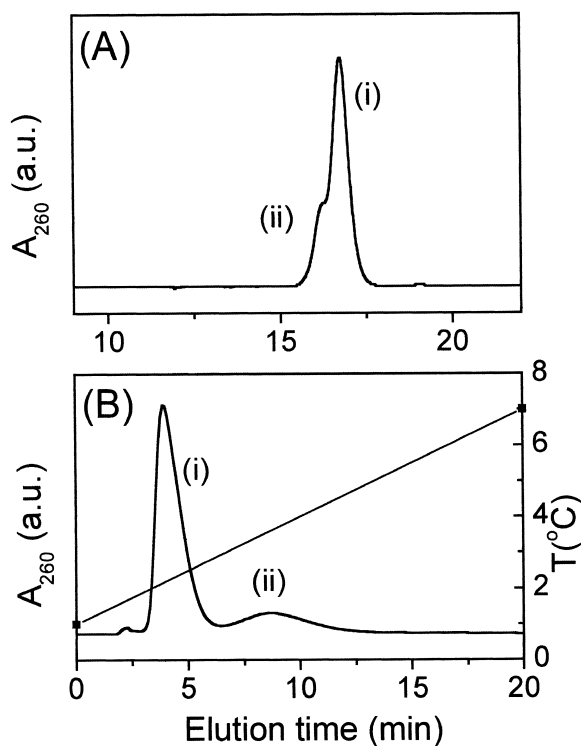

Fig. 1. SEC (A) and RP-TGIC (B) chromatograms of an air terminated polystyryllithium. The SEC chromatogram of the polystyrene product (A) shows the existence of the coupled product as a shoulder (ii) of which the molecular mass is two times as large as the main peak (i). RP-TGIC chromatogram (B) shows higher resolution than SEC but it is not possible to further separate them according to the functional groups.

values of all four different series show a spacing of 104 that corresponds to the molecular mass of the styrene monomer unit. From the molecular mass four series could be inferred as follows.

(1) Normally H-terminated polystyrene: $104.15n$ (n styrene units) $+ 57.12$ (*sec*-butyl anion) $+ 1.01$ (one hydrogen end group) $+ 107.87$ (Ag$^+$), e.g. with $n = 38$ the molar mass of the H-terminated polystyrene was found to be 4123.8 in comparison with the calculated mass of 4123.7.

(2,3) Polystyryl ketone and polystyryl alcohol: their molecular masses differ by 2.0 only and they are not fully resolved due to the isotope effect. Their identification will be elaborated later.

(6) Methoxy end-capped polystyrene: for the degree of polymerization, $n = 38$, the molecular mass of the methoxy end-capped polystyrene was found to
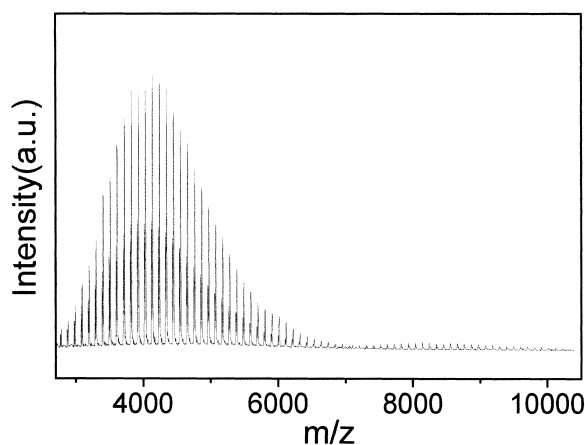
Fig. 2. MALDI-TOF-MS spectra of the polystyrene product shown in Fig. 1. The mass spectrum consists of a major envelope of peaks centered around $m/z = 4500$ and a minor envelope around $m/z = 9000$, of which general feature is consistent with the chromatograms shown in Fig. 1.

be 4154.1 in comparison with the calculated mass of 4153.7.

(7) Carboxylic acid end-capped polystyrene: for the degree of polymerization, $n = 38$, the molecular mass of the carboxylic acid end-capped polystyrene was found to be 4168.3 in comparison with the calculated mass of 4167.7.

In a similar context, we can identify the species in the minor envelope in Fig. 2 from the magnified spectrum shown in Fig. 3B.

(4) Directly coupled polystyrene: for the degree of polymerization, $n = 80$, the molecular mass of the directly coupled polystyrene was found to be 8555.3 compared to the calculated mass of 8554.1.

(5) Dipolystyryl ether: for the degree of polymerization, $n = 80$, the molecular mass of the di-polystyryl ether was found to be 8570.8 compared to the calculated mass of 8570.1.

All the molecular structures of the polymer species identified are summarized in Fig. 4.

Such assignments using the mass spectrum appear reasonable but they need to be confirmed further as exemplified in the difficulty to distinguish polystyryl ketone from polystyryl alcohol. Therefore the separation of individual species was carried out for a detailed analysis. As demonstrated earlier, neither SEC nor RP-TGIC is effective for the purpose. Since most of the functional groups produced from the
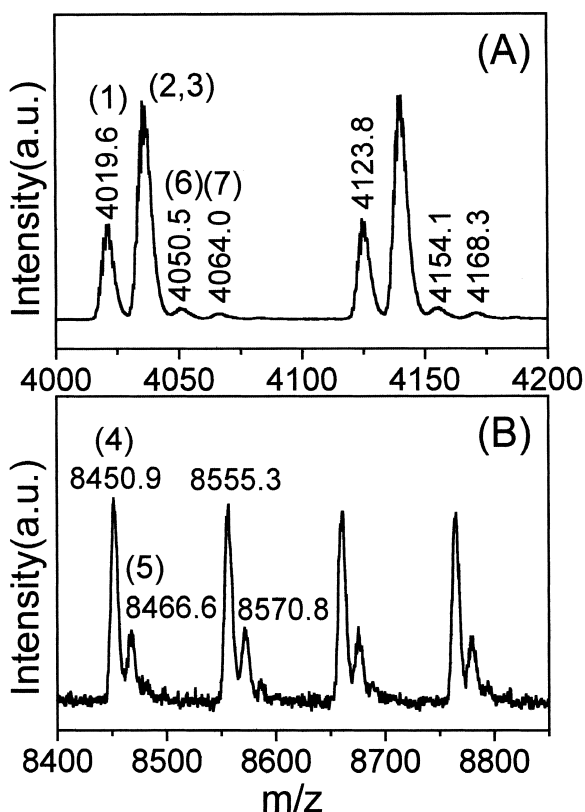

Fig. 3. Magnified mass spectra of Fig. 2. The major envelope (A) actually consists of four different series of the peaks. The m/z values of all four different series of the peaks have a spacing of 104 that corresponds to the molecular mass of the styrene monomer unit. The four species could be identified from their mass as (1) H-terminated polystyrene, (2, 3) polystyryl ketone and polystyryl alcohol, (6) methoxy end-capped polystyrene, and (7) carboxylic acid end-capped polystyrene. The minor envelope (B) contains a species twice the molecular mass of the polystyrenes in the major envelope, (4) directly coupled polystyrene and (5) dipolystyryl ether.

reaction with air are polar, NP-TGIC should be more effective [17]. Mansson reported a successful separation of the products from the reaction of poly-styryllithim with oxygen or carbon dioxide using thin-layer chromatography, silica and light petroleum–CH_2Cl_2 mixture (37.5:62.5 v/v) as the stationary and mobile phases, respectively [8]. We employed similar mobile and stationary phases in NP-TGIC.

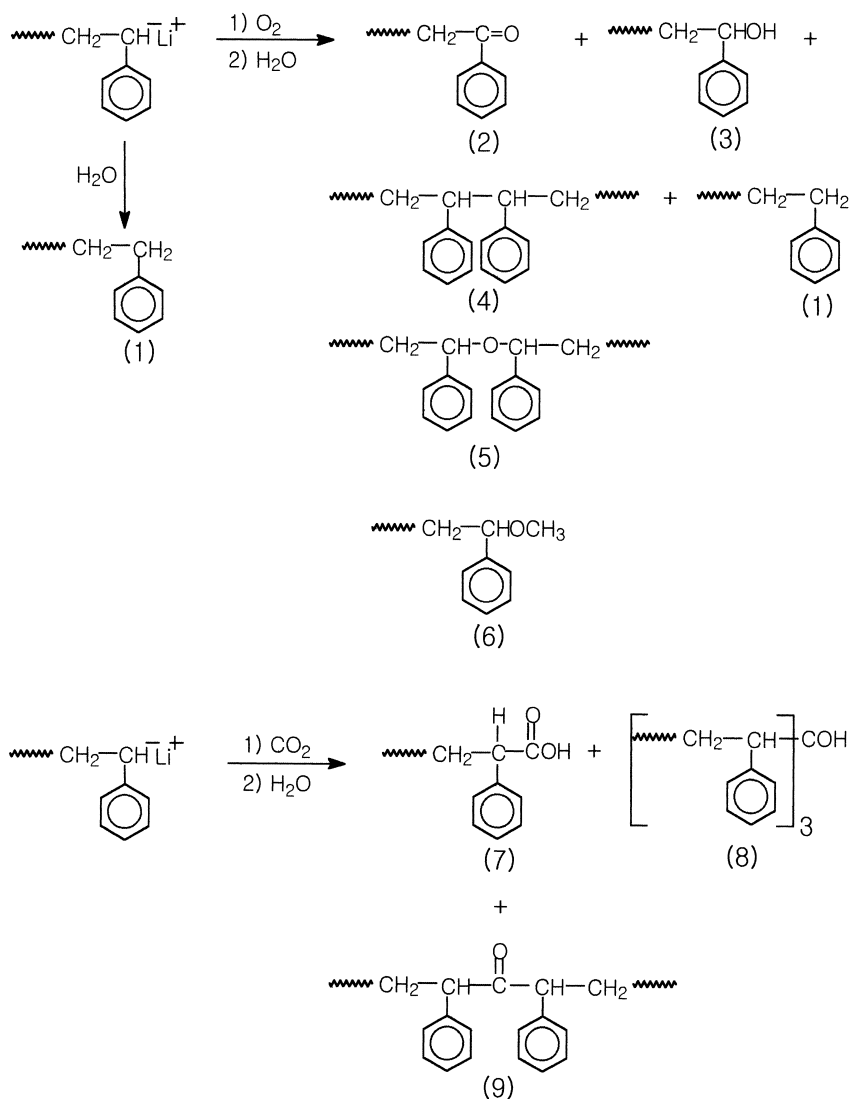Fig. 5 shows the NP-TGIC chromatogram in which more elution peaks are found. The column

Fig. 4. Possible products from the air termination of polystyryllithium.

temperature was changed as shown in the plot. These peaks are fractionated and the fractions of the peaks (2), (3) and (5) are subjected to MALDI-TOF-MS analysis. The results are shown in Fig. 6. The mass spectra of the fractionated samples clearly show the chemical homogeneity and the molecular masses are consistent with the previous analysis results. Therefore we could confirm the presence of the polystyryl ketone (2), polystyryl alcohol (3), and dipolystyryl ether (5). Now the molecular masses of the products (2) and (3) are clearly identified as follows.

(2) Polystyryl ketone: for the degree of polymerization, $n = 38$, the molecular mass of the polystyryl ketone was found to be 4138.1 compared to the calculated mass of 4137.7.

(3) Polystyryl alcohol: for the degree of polymerization, $n = 38$, the molecular mass of the polystyryl alcohol was found to be 4139.0 compared to the calculated mass of 4139.7.

The elution order of (1,4), (2) and (3) is consistent with the R_f value reported by Mansson [8]. However, Mansson did not report the presence of the di-
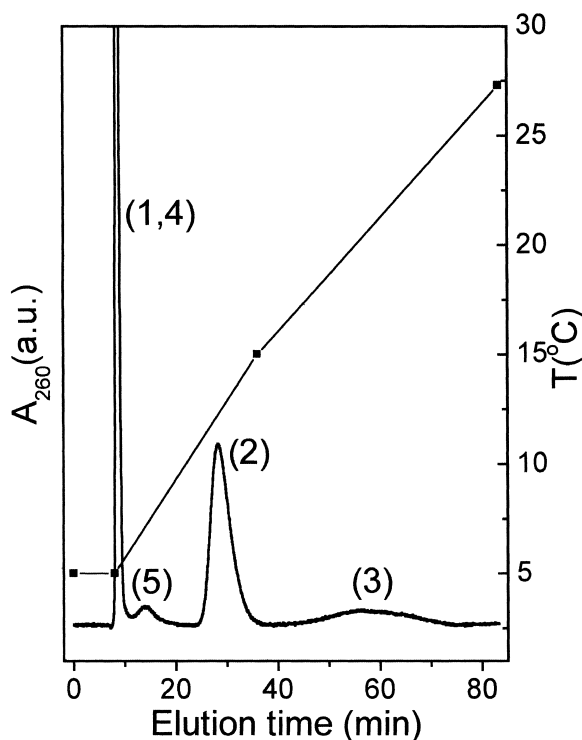
Fig. 5. NP-TGIC chromatogram of the air terminated poly-styryllithium, which shows higher resolution than SEC or RP-TGIC with respect to the functional groups. These peaks are identified from the MALDI-TOF-MS analysis (shown in Fig. 6) as (1,4) H-terminated polystyrene and directly coupled polystyrene, (2) polystyryl ketone, (3) polystyryl alcohol and (5) dipolystyryl ether. The column temperature was changed as in the plot. Column: Nucleosil silica, 100 Å pore, 250×4.6 mm, eluent: light petroleum–CH_2Cl_2 (41:59, v/v).
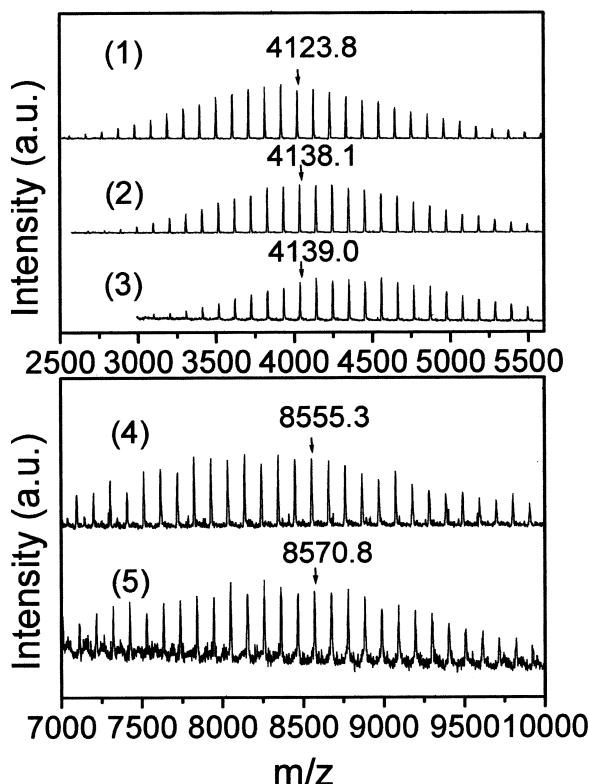

Fig. 6. MALDI-TOF-MS spectra of the fractionated samples by NP-TGIC (shown in Fig. 5). The mass spectra of the fractionated samples clearly show chemical homogeneity and the molecular masses are consistent with the previous identification: (1) H-terminated polystyrene (2) polystyryl ketone (3) polystyryl al-cohol (4) direct coupled polystyrene (5) dipolystyryl ether.

polystyryl ether (5), presumably due to the small amount of the species that escaped from the conven-tional characterization method. The peak (1,4) shows a mass spectrum of a mixture containing H-termi-nated polystyrene and directly coupled polystyrene. The H-terminated polystyrene (1) and directly cou-pled polystyrene (4) differ by a factor of two in molecular mass, but they elute as an unresolved peak since the separation conditions are not appropriate for separation and the amount of the coupled product is small. We could confirm by MALDI-TOF-MS analysis that the retention of the coupled polystyrene (4) is slightly longer than the H-terminated poly-styrene (1) and the coupled polystyrene is enriched at the tail portion of the peak (1,4). The MALDI-

TOF-MS spectra of (1) and (4) in Fig. 6 show the two different molecular mass ranges of a single MALDI-TOF-MS spectrum of the fractionated peak (1,4). Unlike the mass spectrum in Fig. 3B the mass spectra of (1) and (4) in Fig. 6 are free from subsidiary peaks showing that the peak (1,4) consists of the two polymer species only.

In the NP-TGIC separation shown in Fig. 5, we could not find the elution peaks of the carboxylic acid end-capped polystyrene (7) and methoxy end-capped polystyrene (6), which were observed in the MALDI-TOF-MS spectrum in Fig. 3A. The car-boxylic acid end-capped polystyrene (7) is a major product of the CO_2 terminated polystyryllithium [7,10], but the amount of (7) in the polystyrene mixture is small due to the low content of CO_2 in the

air. The carboxylic acid end-capped polystyrene (7) should show a high retention in the NP-TGIC separation due to its polar nature and the peak will be broadened also. The low content of (7) and the peak broadening must have been the reason why it was not identified in the NP-TGIC analysis. The carboxylic acid end-capped polystyrene (7) is the only identified product in this study among the possible products from the reaction of poly-styryllithium with CO_2. Other possible products, trimeric alcohol (8) and dimeric ketone (9) [7,10] were not identified by NP-TGIC or MALDI-TOF-MS, seemingly due to their low contents in the polystyrene mixture. The mechanism of the formation of methoxy end-capped polystyrene (6) needs to be confirmed, but we suspect that it was formed during the quenching the reaction mixture containing radicals with methanol.

To our knowledge, the formation of the di-polystyryl ether (5) is observed for the first time. Mansson earlier observed the partial split of the thin-layer chromatography spot and the spots contained two different molecular mass polystyrenes by SEC analysis [8]. However, it was not possible to distinguish the directly coupled polystyrene (4) from the dipolystyryl ether (5), which could be formed through the reaction of dipolystyryl peroxide with polystyryl lithium [29]. The combination of HPLC and MALDI-TOF-MS was powerful enough to detect such a minor component with relative ease.

In summary we combined two techniques, NP-TGIC and MALDI-TOF-MS, to investigate the products formed from the reaction of polystyryllithium with air. NP-TGIC was employed to fractionate the polystyrene products, namely H-terminated poly-styrene, polystyryl alcohol, polystyryl ketone, direct-coupled polystyrene and dipolystyryl ether, and all of them were identified by the MALDI-TOF-MS analysis. In addition, MALDI-TOF-MS could identify the trace amounts of the minor products, methoxy and carboxylic acid end-capped polystyrenes that could not be detected by the NP-TGIC analysis.

Acknowledgements

References

[1] M. Szwarc, Nature 178 (1956) 1168.
[2] M. Morton, Anionic Polymerization, Principles and Practice, Academic Press, New York, 1983.
[3] P. Rempp, E. Franta, J. Herz, Adv. Polym. Sci. 86 (1988) 147.
[4] M. Van Beylen, S. Bywater, G. Smets, M. Szwarc, D. Worsfold, Adv. Polym. Sci. 86 (1988) 87.
[5] H.L. Hsieh, R.P. Quirk, Anionic Polymerization: Principles and Practical Applications, Marcel Dekker, New York, 1996.
[6] K. Kwon, W. Lee, D. Cho, T. Chang, Korea Polym. J. 7 (1999) 321.
[7] D.P. Wyman, V.R. Allen, J.T. Altares, J. Polym. Sci. A 2 (1964) 4545.
[8] P. Mansson, J. Polym. Sci. Polym. Chem. 18 (1980) 1945.
[9] R.P. Quirk, W.C. Chen, Makromol. Chem. 183 (1982) 2071.
[10] R.P. Quirk, J. Yin, L.J. Fetters, Macromolecules 22 (1989) 85.
[11] M. Aldissi, F. Schue, K. Geckeler, M. Abadie, Makromol. Chem. 181 (1980) 1425.
[12] T. Chang, H.C. Lee, W. Lee, S. Park, C.H. Ko, Macromol. Chem. Phys. 200 (1999) 2188.
[13] H.C. Lee, T. Chang, Polymer 37 (1996) 5747.
[14] W. Lee, H.C. Lee, T. Chang, S.B. Kim, Macromolecules 31 (1998) 344.
[15] W. Lee, H.C. Lee, T. Park, T. Chang, K.H. Chae, Macromol. Chem. Phys. 201 (2000) 320.
[16] H.C. Lee, T. Chang, Macromolecules 29 (1996) 7294.
[17] W. Lee, D. Cho, B.O. Chun, T. Chang, M. Ree, J. Chromatogr. A 910 (2001) 51.
[18] S. Perny, J. Allgaier, D. Cho, W. Lee, T. Chang, Macromolecules 34 (2001) 5408.
[19] H.C. Lee, W. Lee, T. Chang, J.S. Yoon, D.J. Frater, J.W. Mays, Macromolecules 31 (1998) 4114.
[20] H.C. Lee, T. Chang, S. Harville, J.W. Mays, Macromolecules 31 (1998) 690.
[21] D. Cho, S. Park, K. Kwon, T. Chang, J. Roovers, Macromolecules 34 (2001) 7570.
[22] H. Lee, W. Lee, T. Chang, S. Choi, D. Lee, H. Ji, W.K. Nonidez, J.W. Mays, Anal. Chem. 73 (2001) 1726.
[23] M.S. Montaudo, G. Montaudo, Macromolecules 32 (1999) 7015.
[24] M.W.F. Nielen, Mass Spectrom. Rev. 18 (1999) 309.
[25] H. Pasch, R. Ghahary, Macromol. Symp. 152 (2000) 267.
[26] H. Pasch, Adv. Polym. Sci. 150 (2000) 1.
[27] H.J. Rader, W. Schrepp, Acta Polym. 49 (1998) 272.
[28] L.J. Fetters, E.M. Firer, Polymer 18 (1977) 306.
[29] S. Matsugo, I. Saito, in: W. Ando (Ed.), Organic Peroxides, Wiley, New York, 1992, p. 157.