Polymer Bulletin 21, 433–437 (1989)

Polymer Bulletin

Tacticity dependence of thermal degradation of PMMAs with the same chemical structure

Tatsuki Kitayama[1], Hideki Horii[1], Koichi Hatada[1], and Takashi Kashiwagi[2]

[1] Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka, 560 Japan

[2] National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Summary Tacticity dependence of thermal stability of poly(methyl methacrylate)s was examined under nitrogen by differential scanning calorimetric analysis using the isotactic PMMAs prepared with t-C_4H_9MgBr and syndiotactic PMMAs prepared with t-C_4H_9Li-$(C_2H_5)_3Al$ (Al/Li=3), which had the same chemical structure from α-end to ω-end and similar molecular weights. As the molecular weight became smaller, the degradation temperatures of both the isotactic and syndiotactic PMMAs became higher. The syndiotactic PMMAs showed higher degradation temperatures than the isotactic ones with similar molecular weights.

Introduction

Thermal stability of polymer is affected by structural characteristics of the polymer such as chemical structure of monomeric unit, molecular weight, abnormal linkage (e.g. head-to-head or tail-to-tail linkage), and end group structure. Thermal degradation of poly(methyl methacrylate)(PMMA) formed by radical mechanism has been characterized by three different processes;(a) a chain scission initiated at head-to-head linkage, which forms through combination reaction between the polymer radicals, (b) the scission initiated at vinylidene end, which forms through the disproportionation reaction, and (c) a random scission within the main chain (1). This indicates the great influence of irregular structures in the polymer chain upon thermal stability.

Stereochemical structure of the polymer is another important factor affecting properties of polymer. Thermal stability of poly(vinyl chloride) is reported to depend on tacticity (2-6). It is well known that glass transition temperature (T_g) of PMMA strongly depends on the tacticity. The degradation of isotactic and syndiotactic PMMAs was studied by kinetic analysis of monomer formation (7). The isotactic polymer showed higher degradation rates over a range of temperatures from 300 to 400°C, but overall energies of activation for both the polymers were similar to each other. Recently, Chiantore and Guaita (8) reported on the thermal degradation of various PMMAs prepared by anionic polymerization, including an isotactic PMMA. However, the isotactic and syndiotactic PMMAs used in these studies had different molecular weights and different end groups. Since the presence of abnormal structures, structure of end groups and molecular weight affects the thermal stability of PMMA as mentioned above, PMMA samples of different tacticities with the same chemical structure and similar molecular weight are highly desired for the study of the effect of stereoregularity on the thermal stability.

Recently, we found that polymerizations of MMA in toluene at lower temperatures with $t\text{-}C_4H_9MgBr$ (9,10) and with $t\text{-}C_4H_9Li\text{-}R_3Al$ ($Al/Li \geq 3$) (11) gave highly isotactic and syndiotactic PMMAs with narrow molecular weight distribution (MWD), respectively, both of which contained $t\text{-}C_4H_9\text{-}$ group at the α-end and methine proton at the ω-end. Molecular weights of the polymers can be easily controlled by changing the ratio of initiator to monomer. Therefore, these polymer samples meet the above mentioned requirement for the study of thermal stability of PMMA. In this work, thermal degradation of these tactic PMMAs with well-defined structure was studied by differential scanning calorimetry (DSC), and the syndiotactic PMMAs were found to show higher degradation temperature than the isotactic PMMAs with similar molecular weights.

Experimentals

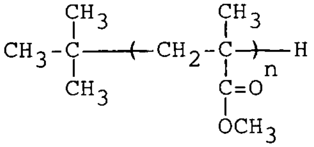
Methyl methacrylate (MMA) and totally deuterated MMA ($MMA\text{-}d_8$) were dried over calcium dihydride and then vacuum distilled.

Polymerization was carried out in a sealed glass ampoule under nitrogen. The reaction mixture was poured into a large amount of hexane to precipitate the polymer formed. The precipitate was collected by filtration, washed several times with hexane, dilute HCl, and water, successively, and dried in vacuo at 50°C.

DSC measurements were performed on a Rigaku Denki DSC 8230 under nitrogen flow (100ml/min) with a heating rate of 5°C/min. The weight of the samples was $0.4 \sim 0.5$mg. A base-line run without a sample was conducted and the resulting data was used to correct the observed DSC curves for polymer samples.

Results and Discussion

Highly isotactic PMMA with narrow MWD was obtained by polymerizing MMA with $t\text{-}C_4H_9MgBr$ in toluene at -78°C. The polymer has one $t\text{-}C_4H_9\text{-}$ group at the α-end and one methine proton at the ω-end as shown below (9,10):



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle OCH_3}{C=O}}{C}}\right)_n-H$$

Highly syndiotactic PMMA with narrow MWD was obtained with $t\text{-}C_4H_9Li\text{-}(C_2H_5)_3Al$ ($Al/Li=3$) in toluene at -78°C (11). The chemical structure of the PMMA is identical to that of the isotactic PMMA prepared with $t\text{-}C_4H_9MgBr$. Number average molecular weights (Mn's) of the isotactic and syndiotactic PMMAs are about 5000, 10000, and 20000.

Table 1 Thermal decomposition of PMMA and poly(MMA-d_8)[a]

Tacticity of PMMA	Initiator	Mn[b]	Mw/Mn[b]	Tacticity(%)[c] I	H	S	T_d[d] (°C)
Syndiotactic	$t\text{-}C_4H_9Li/(C_2H_5)_3Al$	19700	1.30	0	8	92	373
Syndiotactic	$t\text{-}C_4H_9Li/(C_2H_5)_3Al$	10600	1.20	0	10	90	375
Syndiotactic	$t\text{-}C_4H_9Li/(C_2H_5)_3Al$	4800	1.20	0	8	92	379
Syndiotactic[e]	$t\text{-}C_4H_9Li/(C_2H_5)_3Al$	4630	1.21	0[f]	11[f]	89[f]	390
Isotactic	$t\text{-}C_4H_9MgBr$	22000	1.21	96	3	1	368
Isotactic	$t\text{-}C_4H_9MgBr$	9800	1.25	96	3	1	371
Isotactic	$t\text{-}C_4H_9MgBr$	4700	1.13	96	3	1	377
Isotactic[e]	$t\text{-}C_4H_9MgBr$	4730	1.18	98[f]	2[f]	0[f]	382

[a] Polymers were prepared in toluene at -78°C.

[b] Determined by GPC. [c] Determined by ^1H NMR spectroscopy.

[d] Degradation temperature. [e] Poly(MMA-d_8).

[f] Determined by ^{13}C NMR spectroscopy.

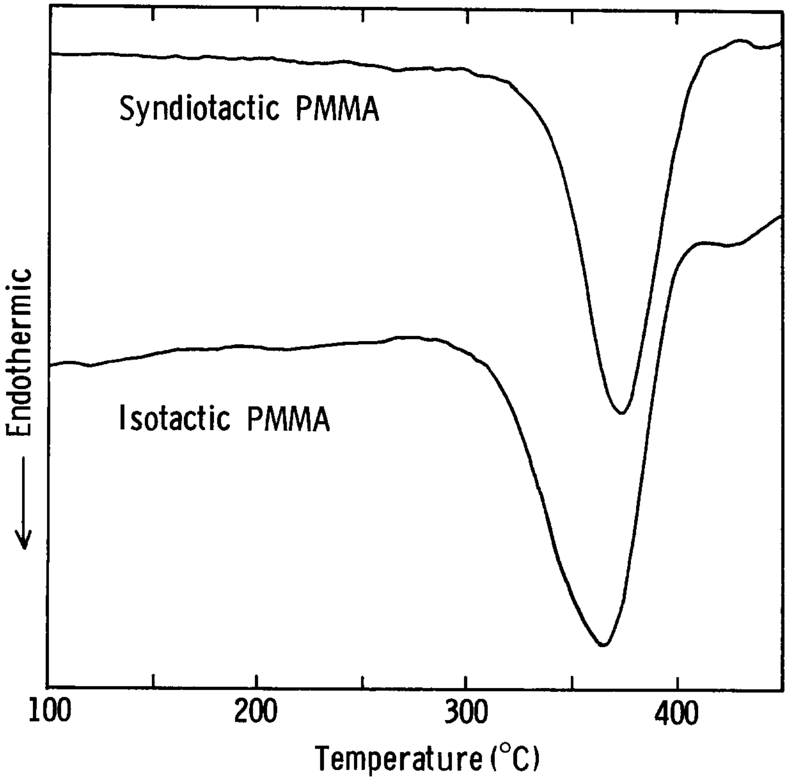


Figure 1 DSC thermograms of isotactic and syndiotactic PMMAs with the same chemical structure
(Heating rate 5°C, nitrogen flow 100mL/min)

Thermal degradation of the isotactic and syndiotactic PMMAs was monitored by the DSC instrument under nitrogen flow. The PMMAs showed single endothermic peaks around 370°C in their DSC thermograms. The thermograms for the isotactic and syndiotactic PMMAs with the Mn of about 20000 are shown in Figure 1 as typical examples. The peak is due to the degradation initiated by the main chain scission (1). There was no sign of oxidative degradation, which should be exothermic. The temperature at the maximum of the endothermic peak was used to characterize the degradation temperature. Standard deviation of the values thus defined was ±1°C for 6 runs. In Table 1 are summarized the degradation temperatures determined in this manner.

The degradation temperatures depended on Mn of the isotactic and syndiotactic PMMAs, and decreased with increasing Mn. Thus, the comparison of the degradation temperatures of the highly tactic PMMAs should be made for the polymers with almost the same Mn. All the syndiotactic PMMAs listed in Table 1 showed higher degradation temperatures than the isotactic PMMAs with the corresponding Mn's. It is therefore concluded that the isotactic PMMA chains thermally degrade more easily than the syndiotactic chains. Chiantone and Guaita (8) reported thermogravimetric (TG) curves for isotactic and syndiotactic PMMAs, whose end group structures were different. The TG curves are slightly different from each other, but not clear enough to show which PMMA is more stable, and the authors did not mention the effect of tacticity on the degradation via the main-chain scission.

Thermal degradation of isotactic and syndiotactic polymers of MMA-d_8 prepared with t-C_4H_9MgBr and t-C_4H_9Li-$(C_2H_5)_3Al$, respectively, was also examined (Table 1). The degradation temperature of the syndiotactic poly(MMA-d_8) was also higher than that of the isotactic polymer, confirming the tacticity dependence of degradation temperature. Both of the isotactic and syndiotactic poly(MMA-d_8)s had higher degradation temperatures than the corresponding undeuterated PMMAs with a similar Mn and MWD. This might be explained by the smaller volume of deuterium than that of hydrogen, namely, the smaller steric repulsion between the substituents along the PMMA chain.

It is reported that isotactic PMMA is more sensitive to electron-beam radiation than syndiotactic one (12), namely, the former degrades more easily than the latter. A similar phenomenon was also reported on poly(α,α-dimethylbenzyl methacrylate)s (13, 14). Therefore, isotactic PMMA is more labile than syndiotactic PMMA both in thermal degradation and radiation-induced degradation processes, even though the mechanism of degradation may be different. It has been evidenced from NMR relaxation experiments that isotactic PMMA chains have higher segmental mobility than syndiotactic chains both in solution (15-20) and in solid state (21, 22). Higher flexibility of the isotactic chains is also reflected in their lower T_g's than those of syndiotactic PMMAs. The difference in the segmental mobility is likely one of the factors causing the difference in thermal stability of syndiotactic and isotactic PMMAs.

Acknowledgment This work was supported in part by a Grant-in-Aid for Scientific Research (No. 62750835) from the Ministry of Education, Science, and Culture, Japan.

References

1)Kashiwagi, T., Inaba, A., Brown, J. E. , Hatada, K., Kitayama, T., Masuda, E., Macromolecules, 19, 2160 (1986).
2)Martinez, G., Mijangos, C., Millan, J., J. Appl. Polym. Sci., 29, 1735 (1984).
3)Martinez, G., Mijangos, C., Millan, J., Polym. Bull., 13, 151 (1985).
4)Martinez, G., Mijangos, C., Millan, J., Eur. Polym. J., 21, 387 (1985).
5)Millan, J., Martinez, G., Mijangos, C., J. Polym. Sci., Polym. Chem. Ed., 23, 1077 (1985).
6)Cuthbertson, M. J., Bowley, H. J., Gerrard, D. L., Maddams, W. L., Shapiro, J. S., Makromol. Chem., 188, 2801 (1987).
7)Jellinek, H. H. G., Luh, M. D., J. Phys. Chem., 70, 3672 (1966).
8)Chiantore, O., Guaita, M., Polym. Bull., 20, 201 (1988).
9)Hatada, K., Ute, K., Tanaka, K., Kitayama, T., Okamoto, Y., Polym. J., 17, 977 (1985).
10)Hatada, K., Ute, K., Tanaka, K., Okamoto, Y., Kitayama, T., Polym. J., 18, 1037 (1986).
11)Kitayama, T., Shinozaki, T., Masuda, E., Yamamoto, M., Hatada, K., Polym. Bull., 20, 505(1988) ; Kitayama, T., Shinozaki, T., Sakamoto, T., Yamamoto, M., Hatada, K., Makromol. Chem. Suppl., submitted.
12)Sharma, V. K., Pethrick, R. A., Affrossman, S., Polymer, 23, 1732 (1982).
13)Hatada, K., Kitayama, T., Danjo, S., Tsubokura, Y., Yuki, H., Morikawa, K., Aritome, H., Namba, S., Polym. Bull., 10, 45 (1983).
14)Hatada, K., Kitayama, T., Okamoto, Y., Yuki, H., Aritome, H., Namba, S., Nate, K., Inoue, T., Yokono, H., ACS Symp. Ser. 266, "Materials for Microlithography", Thompson, L. F., Willson, C. G., Frechet, J. M. J., eds., 399 (1984).
15)Hatada, K., Okamoto, Y., Ohta, K., Yuki, H., J. Polym. Sci., Polym. Lett. Ed., 14,51 (1976).
16)Lyerla Jr., J. R., Horikawa, T. T., J. Polym. Sci., Polym. Lett. Ed., 14, 641 (1976).
17)Lyerla Jr., J. R., Horikawa, T. T., Johnson, D. E., J. Am. Chem. Soc., 99, 2463 (1977).
18)Inoue, Y., Konno, T., Chujo, R., Nishioka, A., Makromol. Chem., 178, 2131 (1977).
19)Hatada, K., Kitayama, T., Okamoto, Y., Ohta, K., Umemura, Y., Yuki, H., Makromol. Chem., 179, 485 (1978).
20)Heatley, F., Cox, M. K., Polymer, 21, 381 (1980).
21)Edzes H. T., Veeman, W. S., Polym. Bull., 5, 525 (1981).
22)Gabrys, B., Horii, F., and Kitamaru, R., Macromolecules, 20, 175 (1987).

Accepted February 21, 1989 S