

Precise Synthesis of a Series of Poly(4-n-alkylstyrene)s and Their Glass Transition Temperatures

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KEYWORDS

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ABSTRACT

Poly(4-n-alkylstyrene)s with 6 kinds of n-alkyl groups such as methyl, ethyl, propyl, butyl, hexyl and octyl groups covering wide molecular weight range from around 5k to over 100k were precisely synthesized by living anionic polymerizations. It was confirmed that all the polymers obtained have narrow molecular weight distribution, i.e., M_w/M_n is all less than 1.1, by SEC. T_g s of all the polymers were estimated by DSC measurements and it turned out to be clear that their molecular weight dependence was well described by the Fox-Flory equations. Furthermore, it is evident that T_g monotonically decreases as a number of carbon atoms of n-alkyl group is increased, though T_g values are all 20 K or more higher than those reported previously for the same polymer series. This is because backbone mobility increases by introducing longer n-alkyl side groups with high mobility, while T_g difference in between this work and the previous one may due to the experimental conditions and also to the molecular weight range adopted.

INTRODUCTION

Various physical properties of polymers are known to be effected by the structures of monomeric units. Physical properties such as glass transition temperature, T_g , plateau modulus, G_N^0 , entanglement molecular weight, M_e , and packing length, p , are very important fundamentals to determine their viscoelasticities and they are kept studying by many researchers¹⁻⁴. In this paper, we focused on T_g by investigating the influence of side chain lengths of polystyrene derivatives.

Nowadays it is well-recognized that glass “transition” is not a thermodynamic phase transition, but a kinetic and relaxation phenomena^{5, 6}. For instance, T_g depends strongly on measurement technique, a temperature changing (heating or cooling) rate and molecular weight, which is generally described by the Fox-Flory equation⁷⁻⁹.

As one category of research on T_g , there are several studies with a focus on n-alkyl chain length of side group in a monomeric unit, such as poly(4-n-alkylstyrene)s¹⁰⁻¹³, poly(n-alkylmethacrylate)s¹⁴⁻²⁵ and poly(n-alkylacrylate)s²⁵. These systematic studies have revealed that T_g of a series of these systematic polymers decrease with increase in the number of carbon for n-alkyl side group. These results can be understood as an enhancement of segment mobility with increasing the number of side chain carbon atoms.

Although there are many reports on physical properties of poly(n-alkylmethacrylate)s¹⁴⁻²⁵, there are few studies on those of poly(4-n-alkylstyrene)s¹⁰⁻¹³. Among them, T_g s of poly(4-n-alkylstyrene)s with a number of n-alkyl carbon atoms from 2 to 18 as a side group was reported by Overberger et al. in 1953¹⁰, while Chapin et al. also investigated T_g s of poly(4-ethylstyrene) and poly(4-n-butylstyrene) in 1962¹¹. Comparing their results, it turned out T_g values reported by Chapin are remarkably higher than those by Overberger. In recent years, T_g s of poly(4-n-alkylstyrene)s with highly stereoregularity were reported. Nakatani et al. revealed polymers synthesized using $TiCl_3$ -TEA catalyst were highly isotactic¹², while Quirk et al. reported polymers obtained with $(Me)_5CpTi(OMe)_3/MAO$

catalyst were highly syndiotactic¹³, the T_g values evaluated in both experiments were higher than those of Overberger. Nakatani et al. and Quirk et al. concluded that these difference in T_g of poly(4-n-alkylstyrene)s was due to the difference in tacticity of polymers. T_g s reported in these articles, however, were close to the results of Chapin et al., whose polymers were synthesized with no catalyst, and hence no regular tacticity is included in the samples. Furthermore it may be conceived that the molecular weights of the samples used in Overberger's work is different from others, though there were no data regarding molecular weight and polydispersity in their study. When one discuss the molecular weight dependence of T_g of polymers, it is quite important and essential to use well-defined polymers concerning molecular weights and polydispersity to reach definite conclusion.

Along this line we synthesized a series of model poly(4-n-alkylstyrene)s having low polydispersity up to higher molecular weight by living anionic polymerizations in this work. More than 4 samples were prepared for one m series, where m denotes the number of carbon atoms in side chains, to clarify the molecular weight dependence of T_g . Then we also compared the present data with the previous ones. The novelty of our work is synthesizing a series of poly(4-substituted styrene)s with narrow polydispersity and covering wide molecular weight range to investigate the effects of the number of substituent carbon atoms on their T_g s.

EXPERIMENTAL SECTION

Materials

4-bromostyrene was purchased from Apollo Scientific Ltd. and purified with vacuum distillation before using. Bromoethane, 1-bromopropane, 1-bromobutane, 1-bromohexane, 4-methylstyrene, 4-n-octylstyrene and Li_2CuCl_4 were purchased from Tokyo Chemical Industry Co., Ltd., while Magnesium was supplied from Kanto Chemical Co., Inc. 4-ethylstyrene, 4-n-propylstyrene, 4-n-butylstyrene and 4-n-hexylstyrene monomers were synthesized by Grignard coupling reactions, the details of synthetic procedures are described below.

THF used for the polymerization of all monomers was distilled under vacuum over anthracene sodium, and then purified by distillation from a solution of α -methyl styrene tetramer disodium salt.

Syntheses of Monomers

4-ethylstyrene monomer was synthesized by the Li_2CuCl_4 -mediated coupling reaction of the Grignard reagent of 4-bromostyrene with bromoethane²⁶. To an ice-cooled THF solution containing bromoethane and Li_2CuCl_4 , the Grignard reagent prepared from 4-bromostyrene and magnesium was added dropwisely over a period of 30 minutes. The resulting reaction mixture was stirred for two days and was then acidified with HCl. Water layer was extracted with diethyl ether. Organic layer was washed with brine and dried over MgSO_4 . After evaporation, the solution was purified with vacuum distillation and colorless liquid was obtained. NMR spectra were shown in Figure S1. ^1H NMR (CDCl_3) δ 7.34 (d, 2H, $J = 8.0$ Hz), 7.16 (d, 2H, $J = 8.0$ Hz), 6.70 (dd, 1H, $J = 10.9, 17.6$ Hz), 5.71 (d, 1H, $J = 17.6$ Hz), 5.19 (d, 1H, $J = 10.9$ Hz), 2.63 (q, 2H, $J = 7.6$ Hz), 1.23 (t, 3H, $J = 7.6$ Hz). ^{13}C NMR (CDCl_3) δ 144.2, 137.1, 135.5, 128.3, 126.6, 113.0, 29.0, 15.9.

4-n-propylstyrene, 4-n-butylstyrene and 4-n-hexylstyrene monomers were synthesized by similar methods as described above for 4-ethylstyrene monomer. NMR spectra were shown in Figures S2-S4.

4-n-propylstyrene: ^1H NMR (CDCl_3) δ 7.33 (d, 2H, $J = 8.0$ Hz), 7.14 (d, 2H, $J = 8.0$ Hz), 6.72 (dd, 1H, $J = 10.8, 17.6$ Hz), 5.71 (d, 1H, $J = 17.6$ Hz), 5.19 (d, 1H, $J = 10.9$ Hz), 2.57 (t, 2H, $J = 7.5$ Hz), 1.63 (m, 2H), 0.95 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3) δ 142.5, 136.8, 135.2, 128.7, 126.2, 112.8, 37.9, 24.6, 13.9.

4-n-butylstyrene: ^1H NMR (CDCl_3) δ 7.33 (d, 2H, $J = 8.1$ Hz), 7.14 (d, 2H, $J = 8.1$ Hz), 6.72 (dd, 1H, $J = 10.9, 17.6$ Hz), 5.71 (d, 1H, $J = 17.6$ Hz), 5.19 (d, 1H, $J = 10.9$ Hz), 2.61 (t, 2H, $J = 12.6$ Hz), 1.58 (m, 2H), 1.34 (m, 2H), 0.93 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (CDCl_3) δ 142.7, 136.8, 135.1, 128.6, 126.2, 112.8, 35.4, 33.6, 22.4, 14.0.

4-n-hexylstyrene: ^1H NMR (CDCl_3) δ 7.31 (d, 2H, $J = 6.2$ Hz), 7.13 (d, 2H, $J = 6.4$ Hz), 6.69 (dd, 1H, $J = 10.9, 17.5$ Hz), 5.71 (d, 1H, $J = 17.6$ Hz), 5.19 (d, 1H, $J = 10.9$ Hz), 2.58 (t, 2H, $J = 7.1$ Hz), 1.60 (m, 2H), 1.30 (m, 6H), 0.88 (t, 3H, $J = 4.4$ Hz). ^{13}C NMR (CDCl_3) δ 142.8, 136.9, 135.2, 128.6, 126.2, 112.8, 35.8, 31.8, 31.5, 29.1, 22.7, 14.1.

Polymerizations

All operations were carried out in sealed glass apparatuses with break-seals under a pressure of 1×10^{-3} Pa or lower. All the monomers were dried over calcium hydride under reduced pressure and purified with n-octylbenzophenone-sodium and then were polymerized by living anionic polymerizations using sec-BuLi as an initiator in THF at -78 °C. The polymers obtained were purified by precipitation from THF solutions into excess amount of methanol. Poly(4-methylstyrene), poly(4-ethylstyrene), poly(4-n-propylstyrene) and poly(4-n-butylstyrene) were obtained as white solids and poly(4-n-hexylstyrene) and poly(4-n-octylstyrene) were obtained as colorless liquids. All samples are coded as PCmSt_X, where m denotes the number of carbon atoms in n-alkyl side group and X does molecular

weight in the unit of kg/mol.

Molecular Characterization

The weight-average molecular weight, M_w , was determined by multi-angle light scattering (MALS) with a Dawn-EOS multi-angle laser light scattering apparatus (Wyatt Technology Co.) in THF, which is a good solvent for all the polymers, at 35 °C. The refractive index increment, dn/dc , of the polymers at 690 nm in THF were estimated at 35 °C using Optilab DSP differential refractometer (Wyatt Technology Co.). The dn/dc values evaluated for PC1St, PC2St, PC3St, PC4St, PC6St and PC8St were 0.179, 0.169, 0.160, 0.158, 0.145 and 0.134, respectively. Polydispersity indices (M_w/M_n) of the polymers were determined by size exclusion chromatography, SEC, using a set of three polystyrene gel columns, G5000HHR of Tosoh Co. or two silica gel columns, KW803 or KW804 of Shodex Co. Appropriate columns and polystyrene standards (1090k, 427k, 96.4k, 37.9k, 9.1k, 5.4k) were utilized in accordance with molecular weight of polymers. THF was used for an eluent at 40 °C and a flow rate was 1 ml/min. ^1H and ^{13}C NMR measurements also supported the successful production of these polymers as shown in Figures S5-S10.

DSC Measurement.

For all the T_g measurements, differential scanning calorimetry (DSC) with a Q2000 calorimeter of TA Instruments inc. was used. Second heating data at a temperature rising rate of 10 K/min was utilized to determine T_g for all the poly(4-n-alkylstyrene) samples. T_g was evaluated as center temperatures between two cross-points of tangent of inflexion point and two baselines as shown in the inset of Figure 2. To investigate heating rate dependence on T_g for the highest molecular weight samples, temperature heating rates of 5 and 2 K/min were also applied. To compare the present results with the previous ones under similar experimental condition, the measurements of a temperature cooling rate of 2 K/min were also

carried out.

RESULTS AND DISCUSSION

Molecular Characteristics

Molecular characteristics of the polymers obtained were summarized in Table 1. The number-average molecular weight, M_n , was calculated by M_w divided by M_w/M_n . The SEC chromatograms of the highest molecular weight sample in each poly(4-n-alkylstyrene) were picked up and shown in Figure 1, while those of the other samples were shown in Figures S11-S16. At least 4 samples with different molecular weight covering wide molecular weight range were synthesized for all poly(4-n-alkylstyrene)s. It was confirmed that the degree of polymerization, DP, which was derived from M_n , of the highest molecular weight polymer in each poly(4-n-alkylstyrene) is larger than 700, and all the polymers have reasonably narrow molecular weight distribution, $M_w/M_n < 1.1$, as shown in Table 1.

TABLE 1 Molecular characteristics of all the polymers.

polymer	$10^{-3}M_n$	$10^{-3}M_w$	DP	M_w/M_n	T_g / K
PC1St_6	6.3	6.4	53	1.01	370.0
PC1St_8	7.7	7.8	66	1.01	373.0
PC1St_14	13.8	14.2	117	1.03	379.1
PC1St_28	27.1	27.6	230	1.02	382.9
PC1St_43	41.3	42.5	350	1.03	384.3
PC1St_107	105	107	890	1.02	385.7
PC1St_177	170	177	1440	1.04	386.2
PC1St_265	250	265	2100	1.06	385.7
PC1St_408	385	408	3260	1.06	386.3
PC2St_4	4.2	4.2	32	1.01	333.1

PC2St_10	9.8	10.0	75	1.02	348.1
PC2St_15	14.9	15.0	110	1.01	352.5
PC2St_24	22.3	23.6	170	1.06	354.9
PC2St_58	57.0	58.1	470	1.02	358.6
PC2St_63	62.1	62.7	430	1.01	358.1
PC2St_362	351	362	2660	1.03	359.4

PC3St_4	3.8	3.9	26	1.02	302.3
PC3St_10	9.8	10.0	67	1.02	318.5
PC3St_18	17.3	17.5	120	1.01	324.4
PC3St_36	35.2	35.9	240	1.02	326.9
PC3St_222	211	222	1440	1.05	330.1

PC4St_8	8.1	8.3	50	1.03	290.3
PC4St_25	24.6	24.8	150	1.01	298.6
PC4St_36	36.0	36.4	220	1.01	299.8
PC4St_49	48.1	49.1	300	1.02	301.1
PC4St_54	52.9	54.0	330	1.02	306.6
PC4St_464	442	464	2760	1.05	304.9

PC6St_4	3.8	3.9	20	1.04	249.8
PC6St_15	14.8	15.1	79	1.02	263.7
PC6St_63	60.6	63.0	320	1.04	268.4
PC6St_140	135	140	710	1.04	268.5

PC8St_3	3.2	3.2	15	1.01	228.5
PC8St_12	11.6	11.7	54	1.01	242.9

PC8St_49	48.4	49.4	220	1.02	248.6
PC8St_129	125	129	580	1.03	250.1
PC8St_717	676	717	3130	1.06	252.6

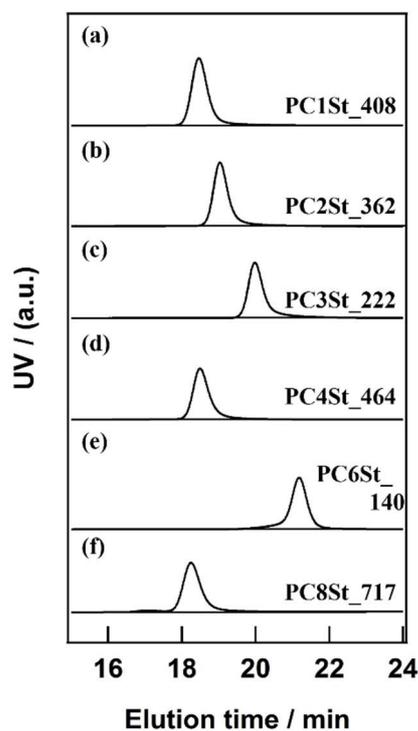


FIGURE 1 SEC chromatograms of the highest molecular weight samples; (a) PC1St_408, (b) PC2St_362, (c) PC3St_222, (d) PC4St_464, (e) PC6St_140 and (f) PC8St_717.

Glass Transition Temperatures

Table 1 also lists the T_g s of all polymers. DSC curves used for the determination of T_g of the polymers were shown in Figure 2 and in Figures S17-S22. The heating rate dependence

of T_g s of the highest molecular weight samples were shown in Figure S23. Figure 3 shows the molecular weight dependence of the glass transition temperatures for all poly(4-n-alkylstyrene)s. It is obvious that the T_g s of a series of polymers increase as the molecular weight and finally they reach asymptotic values at high molecular weight. The similar molecular weight dependence was also reported for polystyrene (PS) and poly(dimethyl siloxane) and others in literatures^{18, 27-31}. It is well-established that the molecular weight dependence of T_g can be described by the following empirical Fox-Flory equation⁷⁻⁹

$$T_g(M_n) = T_{g,\infty} - \frac{K}{M_n}$$

where the $T_{g,\infty}$ is the T_g at infinitely high molecular weight and K is polymer-specific constant. Glass transition temperatures for a series of polymers were described by the Fox-Flory equations well as shown in Figure 3 (solid lines). This equation is known to be applicable only for high molecular weight samples, but not for the molecules with low molecular weights^{9, 27, 32}, therefor the Ueberreiter-Kaing equation was introduced^{32, 33}. Table 2 summarizes the T_g values of the highest molecular weight samples together with the Fox-Flory fitting parameters, $T_{g,\infty}$ and K . K values of all poly(4-n-alkylstyrene)s were estimated to be approximately in the order of 100 K kg mol⁻¹, indicating that the molecular weight dependence of T_g for these polymers is similar. To discuss the universality of T_g s for the present samples, Figure 4 shows a degree of polymerization dependence of the normalized glass transition temperature, $T_g/T_{g,\infty}$, for all polymers together with the data for PS (T_g s of PS were shown in Figure S24). Interestingly, all the data are on a pseudo universal curve suggesting that the molecular weight dependence of T_g s can be determined by the basic chemical architecture of monomer, i.e., styrene in the present case.

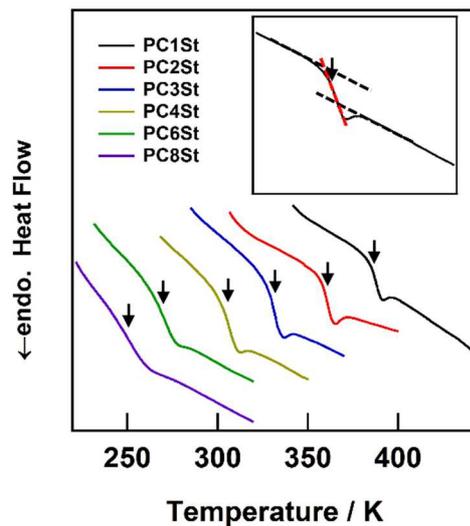


FIGURE 2 DSC curves of PC1St₄₀₈ (black), PC2St₃₆₂ (red), PC3St₂₂₂ (blue), PC4St₄₆₄ (yellow), PC6St₁₄₀ (green) and PC8St₇₁₇ (purple). Arrows denote glass transition temperatures. The inset shows how to determine a T_g .

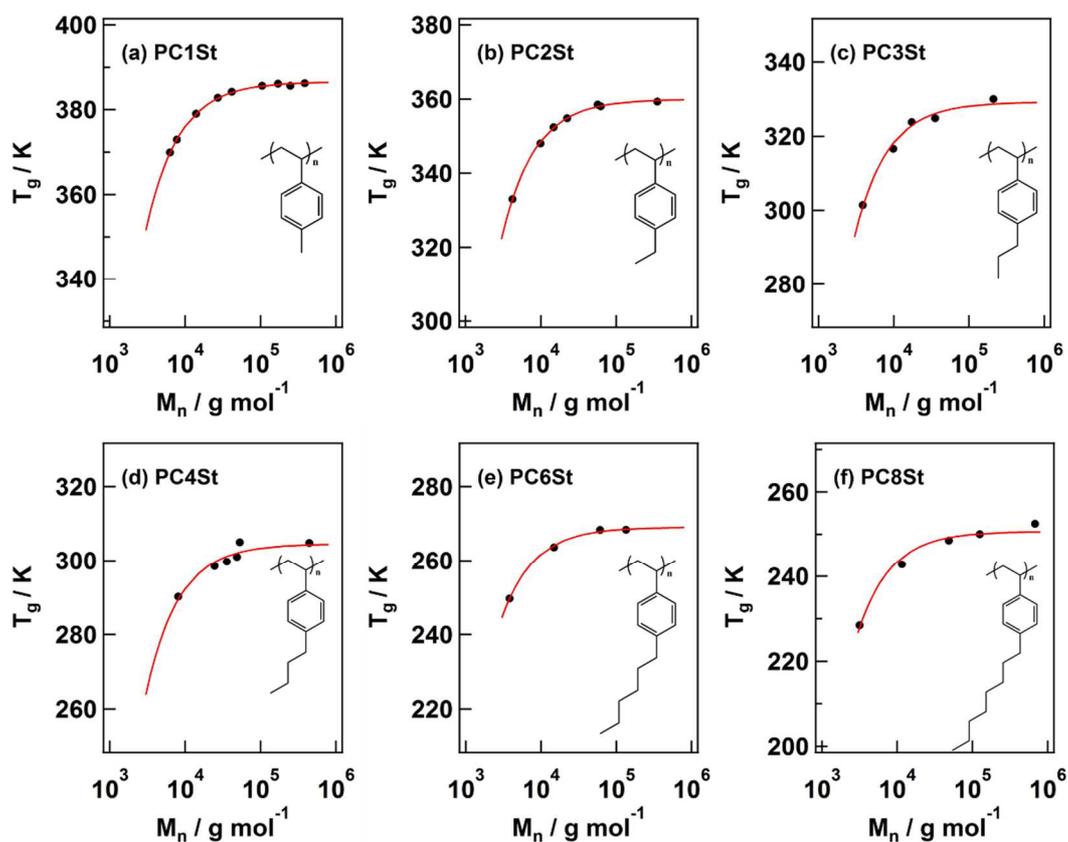


FIGURE 3 Molecular weight dependence of T_g s of all the polymer samples; (a) PC1St, (b) PC2St, (c) PC3St, (d) PC4St, (e) PC6St and (f) PC8St.

TABLE 2 T_g s of the highest molecular weight samples and fitting parameters $T_{g,\infty}$ and K in the Fox-Flory equations.

polymer	T_g / K	$T_{g,\infty} / K$	$K / K \text{ kg mol}^{-1}$
PC1St_408	386.3	386.8	105
PC2St_362	359.4	360.0	113
PC3St_222	330.1	329.3	109
PC4St_464	304.9	305.0	122
PC6St_140	268.5	269.1	74

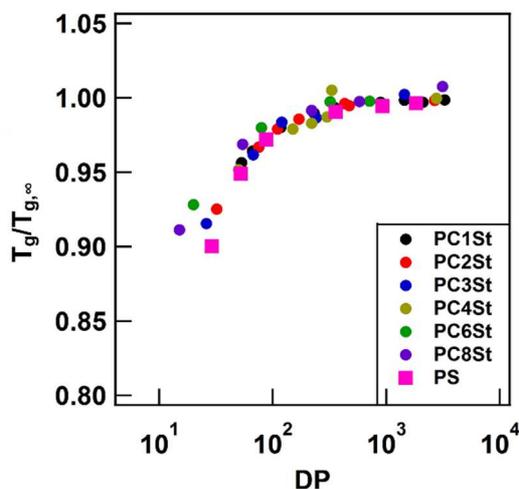


FIGURE 4 Relationship between degree of polymerization and the normalized temperatures, $T_g/T_{g,\infty}$, for all the polymers; PC1St (black filled circle), PC2St (red filled circle), PC3St (blue filled circle), PC4St (yellow filled circle), PC6St (green filled circle), PC8St (purple filled circle), PS (pink filled square).

T_g s of the highest molecular weight samples were compared in Figure 5, where the data for PS, 377 K, was also plotted here. Though T_g of PC1St, 386 K, is higher than that of PS, T_g s of the other all polystyrene derivatives are evidently lower than that of PS and they are decreasing monotonically with increase in a number of carbon atoms on n-alkyl side group within the scope of our experiment. These results are qualitatively similar to the results of Overberger et al.,¹⁰ and poly(n-alkylmethacrylate)s¹⁸. This is because backbone mobility becomes high by introducing n-alkyl groups with high mobilities on para site, i.e., the segment mobility increases by this chemical structural modification. Along this line, the fact that T_g of PC1St is higher than that of PS is an exception. There must be a reason for this, it

could be due to segment mobility, i.e., it is less affected by small methyl group, it rather contribute to rigid backbone bulkiness instead and simply increase the monomer mass.

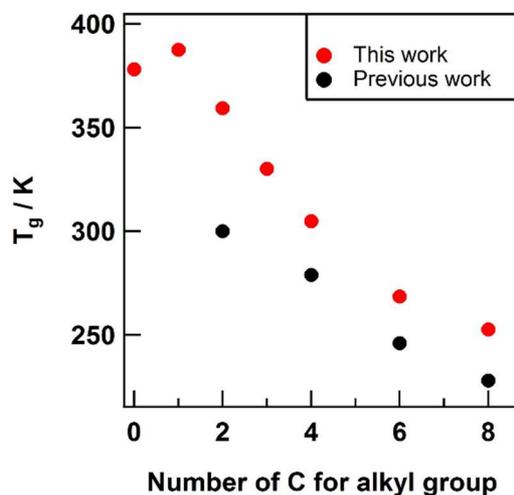


FIGURE 5 T_g variation dependent on the number of n-alkyl carbon atom for the present work (red filled circle) in comparison with the data reported in the previous work (black filled circle)¹⁰.

Here, we compared the results evaluated in this work with those obtained in the previous report¹⁰. It is obvious that T_g s evaluated in this work are much higher than those of the previous report. There exists 60 K difference for PC2St and also approximately 25 K difference for PC4St, PC6St and PC8St in between two experiments.

Two major reasons can be conceived to explain the difference in T_g . The first one is consisted of the experimental conditions, the second one could be the difference in molecular weight range.

Firstly experimental conditions should be considered. Glass transition is a kinetic phenomenon, so that T_g depends crucially on experimental techniques accompanied by

heating and cooling rate^{5,6}. In this work, the T_g s were determined by DSC measurements at a temperature heating rate of 10 K/min, while Overberger et al. obtained the T_g s by the refractometric method at a temperature cooling rate of around 2 K/min. This difference can give large effect on T_g values, then we evaluated T_g s at a cooling rate of 2 K/min, which is the same rate as the one adopted in the previous work¹⁰. The results are also listed in Table 3. Though some drops in several degrees can be recognized, there left large difference in spite of adopting the same temperature cooling rate. Interestingly, however, T_g values reported in the literature (Ref. #10) were approximately agree with the temperatures at crossing points of the endotherm heat drop and baselines on the DSC curves as shown in Figure S25 at a cooling rate of 2 K/min. T_g values evaluated by the refractometric method might be corresponded with not the medium points as adopted in this work but the heat drop end points.

TABLE 3 Glass transition temperatures of the highest molecular weight polymer samples measured by different conditions.

polymer	T_g / K ^a	$T_{g,2K} / K$ ^b	$T_{g,pre} / K$ ^c
PC1St_408	386.3	n.d.	n.d.
PC2St_362	359.4	353.2	300
PC3St_222	330.1	326.0	n.d.
PC4St_464	304.9	298.7	279
PC6St_140	268.5	260.5	246
PC8St_717	252.6	244.1	228

^a T_g at a temperature heating rate of 10 K/min determined by DSC. ^b T_g at a cooling rate of 2 K/min determined by DSC. ^c T_g at a cooling rate of around 2 K/min determined by the

refractometric method in the previous work¹⁰.

Second reason is due to molecular weight range and molecular weight distribution. All the polymers used in this report were synthesized by living anionic polymerizations, so that they are all guaranteed to have high molecular weight and narrow polydispersity. On the other hand, there was no information about molecular weight and polydispersity for all samples in the previous report⁹. Taking the molecular weight dependence of T_g s expressed by the Fox-Flory equations as shown in Figure 3 into account, it is conceivable that the molecular weights of some samples used in the previous work are fairly low.

Finally we also discuss the achievements reported in the other previous works^{12, 13}. As mentioned in the introduction section, their samples have high isotactic or syndiotactic moieties, while all the samples adopted in this work have no tacticity since they were synthesized with no catalyst such as Ziegler-Natta. Nevertheless, the present T_g values were approximately similar to those of the previous works¹¹⁻¹³. It has been reported that the tacticity has influence on T_g s of poly(α -methylstyrene) and poly(methylmethacrylate), but not on those of PS and polymethylacrylate⁶. We considered that T_g s of poly(4-n-alkylstyrene)s were also independent of its tacticity. We are continuing the studies on the solution properties and viscoelasticity of the present polymers, especially packing length will be focused soon.

CONCLUSION

A series of poly(4-n-alkylstyrene)s with different number of carbon atoms in n-alkyl side groups, methyl, ethyl, propyl, butyl, hexyl and octyl groups, were precisely synthesized via living anionic polymerizations covering wide molecular weight range. M_w and M_w/M_n of all samples were determined by MALS and SEC, respectively, and their M_w/M_n were confirmed to be all lower than 1.1. T_g s were estimated by DSC measurements, their molecular weight dependence was confirmed to be well described by the Fox-Flory empirical equations. It has been found that T_g decreases with increasing the number of carbon atoms in n-alkyl side chain. This tendency was qualitatively in good agreement with the previous reports for n-alkyl-substituted polymers. T_g s evaluated in this work, however, are 20 K or more higher than those reported in the previous work. This discrepancy is due to the difference in the molecular weight range of samples and also in experimental conditions adopted in two works.

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GRAPHICAL ABSTRACT

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Precise Synthesis of a Series of Poly(4-n-alkylstyrene)s and Their Glass Transition Temperatures

Poly(4-n-alkylstyrene)s with 6 kinds of n-alkyl groups such as methyl, ethyl, propyl, butyl, hexyl and octyl groups covering wide molecular weight range from around 5k to over 100k were precisely synthesized by living anionic polymerizations. The molecular weight dependence of T_g s of all the series was expressed by the Fox-Flory equations and they were found to be decreased with n-alkyl carbon atoms on side chains.

