Macromolecules

Volume 24, Number 17 August 19, 1991

Effect of Alkyl Chain Length on the Polymerization Thermodynamics of 2-Amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines by Means of DSC

Hideo Kunisada,* Yasuo Yuki, and Shuji Kondo

Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Received April 12, 1990; Revised Manuscript Received March 21, 1991

ABSTRACT: Thermal polymerization of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines was investigated by differential scanning calorimetry (DSC). Alkyl groups of the monomers were propyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and docosyl groups. A polymerization exotherm was observed in DSC curves above the melting point for the monomers having alkyl groups below 16 carbon numbers. The ceiling temperature (T_c) and heat of polymerization (ΔH_p) were determined from the exothermic peaks in DSC curves. The T_c and the ΔH_p values decreased with an increasing number of carbon atoms in the alkyl groups of the monomers. T_c and ΔH_p were also obtained from the equilibrium monomer concentration, which was determined by isothermal polymerization using DSC.

Introduction

Thermodynamic parameters of polymerization, such as ceiling temperature, heat of polymerization, and entropy of polymerization, have been determined by various methods for many monomers. One of the most convenient and direct methods to follow the polymerization reaction is differential scanning calorimetry (DSC). Horie et al.[1] determined the heat of polymerization for styrene and methyl methacrylate by isothermal DSC and found that the values were in good agreement with the conventional values. Kishore et al.[2-4] investigated the thermal polymerization of acrylamide in the molten state by a dynamic DSC technique and obtained the thermodynamic and the kinetic parameters. Malavašič et al.[5] reported the heat of polymerization and the overall activation energies for methacrylic acid and alkyl methacrylates by isothermal bulk polymerization. We found that the ceiling temperature of isopropenyl-1,3,5-triazines could be determined easily by a dynamic DSC technique.[6,7] However, few systematic studies on the relation between the structure of the monomers and the thermodynamic parameters of polymerization have been reported.

In a series of studies on the polymerization thermodynamics of isopropenyl-1,3,5-triazines, we observed that the ceiling temperature and the heat of polymerization depend on the steric effects and electronic effects of the substituents.[8-13]

Isopropenyltriazines are suitable for systematic investigation on the thermodynamics of polymerization, because the monomers can be easily polymerized without an initiator after melting and various substituents can readily be introduced to them. In order to obtain the information about the steric effects on the thermodynamics of polymerization more clearly, the thermal polymerization of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines is investigated by means of DSC. This paper deals with the influence of the length of the alkyl group on the thermodynamic parameters of polymerization. The solution polymerization of these monomers and the thermal properties of the resulting polymers were already reported previously.[14]

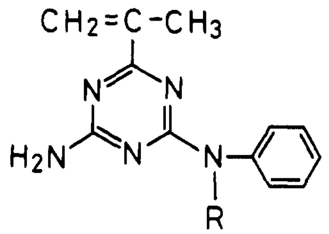
Experimental Section

Monomers. 2-Amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines (N3, N6, N8, N10, N12, N14, N16, N18, and N22) were prepared by an alkylation reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine with alkyl bromides as described in a previous paper.[14] The structure and the abbreviation of the monomers used in this study are shown in Figure 1.

Thermal Polymerization. The course of the thermal polymerization of the monomers was followed by the measurement of DSC on a Rigaku Denki DSC-8230. A 1–4-mg monomer was accurately weighed and taken in an aluminum pan covered with a lid. The heating rate was varied from 1.25 to 20 °C/min. The heat of fusion and the apparent heat of polymerization were calculated from the areas of DSC curves. Indium (mp 156.4 °C, ΔH_m = 28.41 J/g) was used as the standard for the calibration of the temperature and heat energy.

Isothermal polymerization was carried out by using DSC operated isothermally. After the DSC was held at the prescribed

0024-9297/91/2224-4733$02.50/0



R = n-C_3H_7 (N3), n-C_6H_{13} (N6), n-C_8H_{17} (N8),
n-$C_{10}H_{21}$ (N10), n-$C_{12}H_{25}$ (N12), n-$C_{14}H_{29}$ (N14),
n-$C_{16}H_{33}$ (N16), n-$C_{18}H_{37}$ (N18), n-$C_{22}H_{45}$ (N22)

Figure 1. Structure and abbreviations of isopropenyl-1,3,5-triazines.

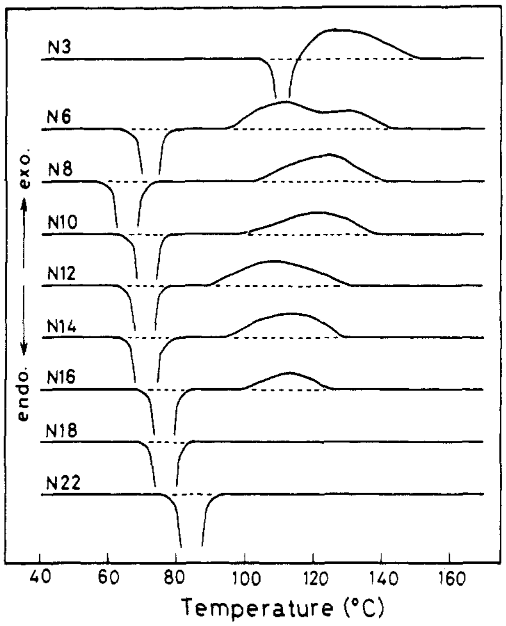


Figure 2. DSC curves of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines (N3–N22) at the heating rate of 5 °C/min.

temperature, a 2-mg monomer was set quickly on the DSC and polymerized for 1.5–3 h.

After a thermal polymerization, the residual monomer content was determined by ultraviolet spectrometry. A Hitachi EPS-3T type spectrophotometer was used for determining the absorbance at 217 nm for the extracted monomer in ethanol. The conversion of the thermal polymerization was calculated from the residual monomer content. The calculation was based on the assumption that weight loss of sample was due to vaporization of the monomer and occurred at high temperature. The weight loss was less than 1% for all polymerizations.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Tosoh HLC-803D with G2000H, G3000H, and GMH TSK gel columns and a differential refractometric detector in tetrahydrofuran. The columns were calibrated with a set of monodisperse polystyrene standards.

Results and Discussion

Thermodynamics of Polymerization by Dynamic DSC. DSC measurements of isopropenyl-1,3,5-triazines were carried out at various heating rates. Figure 2 shows typical DSC curves at the heating rate of 5 °C/min. Melting endothermic peaks were observed at 60–110 °C for all monomers. The melting points (mp) and the heats of fusion (ΔH_m) were determined from the endothermic peaks. These values at the various heating rates are shown in Table I. The ΔH_m values are almost constant regardless of the heating rate. The entropy of fusion (ΔS_m) calculated from the mp and mean of the ΔH_m is also shown in Table I. Table I includes the previous results for the monomers such as 2-amino-4-(*N*-methyl- (N1), *N*-ethyl- (N2), and *N*-butyl- (N4) anilino)-6-isopropenyl-1,3,5-triazine.[10] The relationships between the thermodynamic parameters of fusion (mp, ΔH_m, and ΔS_m) and the carbon numbers in the alkyl group of the monomer are illustrated in Figure 3. For the monomers containing an alkyl group up to 6 or 8 carbon numbers, the mp and ΔH_m decreased with an increase of the carbon numbers. They would be due to the decrease in the intermolecular interaction such as hydrogen bonding of an amino group with a nitrogen atom in a triazine ring; that is, the blocking effect of the alkyl group on the interaction would become larger as the chain length increased. On the other hand, the ΔH_m increased with increasing carbon numbers for the monomers having more than 10 carbon numbers of the alkyl group. In this carbon numbers region, the monomer would be mainly crystallized in alkyl chain packing. The ΔS_m also increased with the length of the alkyl group in a similar manner as the ΔH_m at this carbon numbers region, which results in the fact that the mp change is not very clear for N10–N22.

Polymerization of an exothermic peak was observed in the DSC curves (Figure 2) above the melting point for N3–N16. An apparent heat of polymerization ($\Delta H_p'$) can be obtained from the area of the exothermic peak. Because the polymerization exotherm is close to the melting endotherm in the DSC curve of N3, there is a possibility that both peaks compensate each other. The lower heating rate gives higher conversion and consequently leads to greater polymerization of the exothermic peak. In addition, because the initiation of polymerization shifts to low temperature at a lower heating rate, the exothermic peak approaches the endothermic peak. Therefore, when the compensation occurred, its degree should increase with a decreasing heating rate. However, since the ΔH_m of N3 was constant regardless of the heating rate, as well as the other monomers as mentioned above, the compensation of both peaks can be neglected in the calculation of the heat of polymerization. The values of $\Delta H_p'$ are shown in Table I together with the final temperature of the polymerization exothermic peaks (T_f).

After the thermal polymerization, the conversion was obtained from the residual monomer content determined by ultraviolet spectrometry. Both the $\Delta H_p'$ and the conversion decrease with an increasing heating rate. The heat of polymerization (ΔH_p) can be calculated from the $\Delta H_p'$ and the conversion. The ΔH_p values are almost constant regardless of the heating rate in each monomer as shown in Table I. The ΔH_p of N3–N16 are summarized in Table I as the average value together with the values of previous monomers.

In Figure 2, the polymerization exotherm of N6 shows a prominent shoulder in the late stage of the exotherm. A similar behavior was observed in the case of high conversion such as N3 at 1.25 and 2.5 °C/min, N6 at 1.25 and 2.5 °C/min, N10 at 1.25 °C/min, and N14 at 1.25 °C/min. An ultraviolet spectrum of the extract from the polymerization mixture in ethanol agreed completely with that of the monomer for each case. This indicates that formation of ethanol-soluble byproducts did not occur during the polymerization. Horie et al.[1] and Malavašič et al.[5] reported that the polymerization rate was accelerated by a gel effect at the later stage of isothermal bulk polymerization for alkyl methacrylates or styrene measured by DSC. Number-average molecular weights of poly(N6) determined by GPC were 13.3 × 10^4 (heating rate, 1.25 °C/min), 13.1 × 10^4 (2.5 °C/min), 11.4 × 10^4 (5 °C/min), 8.7 × 10^4 (10 °C/min), and 8.1 × 10^4 (20 °C/min), respectively. The molecular weights of the polymers

Table I
Thermal Behaviors of Isopropenyl-1,3,5-triazines Determined by DSC

monomer	heating rate, °C/min	mp, °C	ΔH_m, kJ/mol	T_f,[a] °C	$-\Delta H_p'$,[b] kJ/mol	convn, %	$-\Delta H_p$,[c] kJ/mol	ΔS_m, J/K·mol	$-\Delta S_p°$, J/K·mol
N3	1.25	107	31.88	140	29.79	66.0	45.1		
	2.5	107	31.34	147	18.07	39.6	45.6		
	5.0	107	31.21	148	18.33	39.5	46.4		
	10.0	107	31.80	153	11.17	25.0	44.7		
	20.0	107	31.42	157	6.95	14.8	47.0		
			(31.5 ± 0.3)[d]	(157)[e]			(45.8 ± 0.9)[d]	82.9 ± 0.8	117.4 ± 2.1
N6	1.25	68	24.39	123	29.29	67.3	43.5		
	2.5	68	24.18	126	27.82	64.0	43.5		
	5.0	68	24.02	142	20.71	48.4	42.8		
	10.0	68	23.85	144	18.54	42.9	43.2		
	20.0	68	23.85	149	13.72	32.0	42.9		
			(24.1 ± 0.2)[d]	(149)[e]			(43.2 ± 0.3)[d]	70.6 ± 0.6	112.0 ± 0.7
N8	1.25	61	24.43	132	17.74	41.9	42.3		
	2.5	61	24.35	135	15.73	37.9	41.5		
	5.0	61	24.52	137	10.21	23.9	42.7		
	10.0	61	24.98	140	3.43	8.0	42.9		
	20.0	61	24.89	143	2.05	5.0	41.0		
			(24.6 ± 0.3)[d]	(143)[e]			(42.1 ± 0.8)[d]	73.6 ± 0.9	110.1 ± 1.9
N10	1.25	67	32.30	133	26.94	64.9	41.5		
	2.5	67	32.51	136	12.64	31.2	40.5		
	5.0	67	32.09	137	9.04	21.5	42.0		
	10.0	67	31.84	138	7.57	18.2	41.6		
	20.0	67	32.47	140	4.90	11.8	41.5		
			(32.2 ± 0.3)[d]	(140)[e]			(41.4 ± 0.6)[d]	94.7 ± 0.9	108.5 ± 1.5
N12	1.25	66	41.13	126	23.85	58.2	41.0		
	2.5	66	41.13	129	13.22	32.1	41.2		
	5.0	66	41.51	130	11.13	26.8	41.5		
	10.0	66	40.96	132	8.91	21.3	41.8		
	20.0	66	40.46	134	0.96	2.4	40.0		
			(41.0 ± 0.4)[d]	(134)[e]			(41.1 ± 0.7)[d]	120.9 ± 1.2	108.7 ± 1.7
N14	1.25	66	46.23	120	27.95	70.6	39.6		
	2.5	66	45.56	125	20.04	50.9	39.4		
	5.0	66	45.19	127	12.51	32.5	38.5		
	10.0	66	45.65	130	4.23	10.5	40.3		
	20.0	66	46.23	132	2.18	5.4	40.4		
			(45.8 ± 0.5)[d]	(132)[e]			(39.6 ± 0.8)[d]	135.0 ± 1.5	104.9 ± 2.0
N16	1.25	72	51.21	125	10.96	28.9	37.9		
	2.5	72	51.13	127	4.64	11.9	39.0		
	5.0	72	51.46	128	5.44	13.9	39.1		
	10.0	72	52.09	130	1.34	3.5	38.3		
	20.0	72	51.84	[f]					
			(51.5 ± 0.4)[d]	(130)[e]			(38.6 ± 0.6)[d]	149.2 ± 1.2	102.4 ± 1.5
N18	5.0	72	60.71					175.9	
N22	5.0	80	74.14					209.8	
N1[g]		118	31.4	(166)[e]			50.2	80.3	126.1
N2[h]		107	27.6	(163)[e]			46.9	72.6	118.9
N4[i]		78	31.8	(157)[e]			42.7	90.6	110.2

[a] Final temperature of the polymerization exothermic peak. [b] Apparent heat of polymerization obtained from the exothermic peak. [c] Heat of polymerization calculated from $\Delta H_p'$ and conversion. [d] The mean value. [e] Ceiling temperature (T_c). [f] Polymerization exothermic peak was not observed in the DSC curve. [g] 2-Amino-4-(*N*-methylanilino)-6-isopropenyl-1,3,5-triazine.[8] [h] 2-Amino-4-(*N*-ethylanilino)-6-isopropenyl-1,3,5-triazine.[17] [i] 2-Amino-4-(*N*-butylanilino)-6-isopropenyl-1,3,5-triazine.[17]

obtained at lower heating rates were greater than those at higher heating rates; that is, the polymerization exotherm having a shoulder gave the polymer with a higher molecular weight. Further, no difference in their infrared spectra could be detected in these polymers. Therefore, the shoulder in the polymerization exotherm of the present monomers would be caused by the gel effect.

Although the monomer still remains abundant, the thermal polymerization is terminated at T_f as shown in Table I. This is due to the limitation of polymerization by the ceiling temperature. In the previous papers,[6,7] we found that the final temperature of polymerization of an exothermic peak in a DSC curve for isopropenyl-1,3,5-triazines could be approximated to the ceiling temperature when the polymerization terminated at low conversion. The ceiling temperature (T_c) of the present monomers was also determined according to the above information. The T_f at the lowest conversion, that is, the T_f at the heating rate of 20 °C/min except for N16, which is at 10 °C/min, approximated to the T_c in bulk as listed in Table I. The error in temperature of the DSC measurement at 20 °C/min was determined to be within 0.5 °C by measurement of indium as the standard sample for the calibration. The conversion of N6 at 20 °C/min, which was 32%, might be too high to estimate T_c. A heating rate faster than 20 °C/min might give a better estimation. However, because the faster rate leads to a large error in temperature and heat energy, DSC measurement was carried out at the heating rate of below 20 °C/min in this study.

The thermodynamic equation of polymerization is expressed as[15]

$$\ln [M]_e = \frac{\Delta H_p}{RT_c} - \frac{\Delta S_p°}{R} \qquad (1)$$

where $[M]_e$, R, and $\Delta S_p°$ denote the equilibrium monomer concentration (mol/L), the gas constant, and the entropy change of polymerization, respectively. If the specific gravity of the monomer in the molten state (s) is assumed

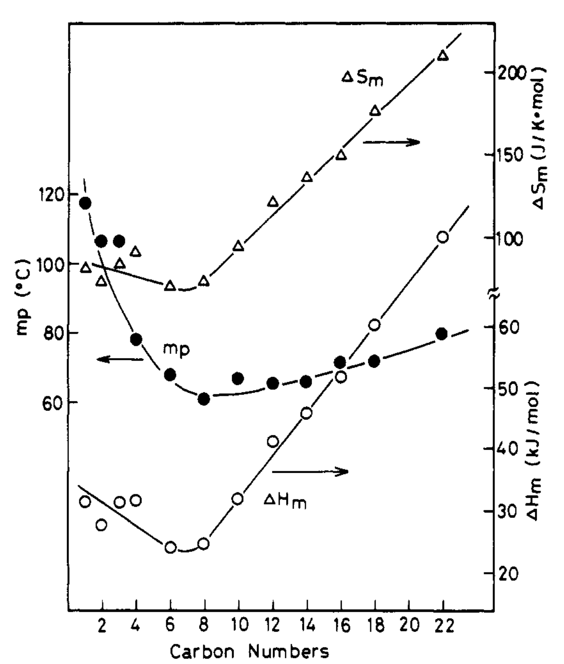


Figure 3. Relationship between the carbon numbers in the alkyl group of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines and thermodynamic parameters of fusion: (●) mp; (○) ΔH_m; (△) ΔS_m.

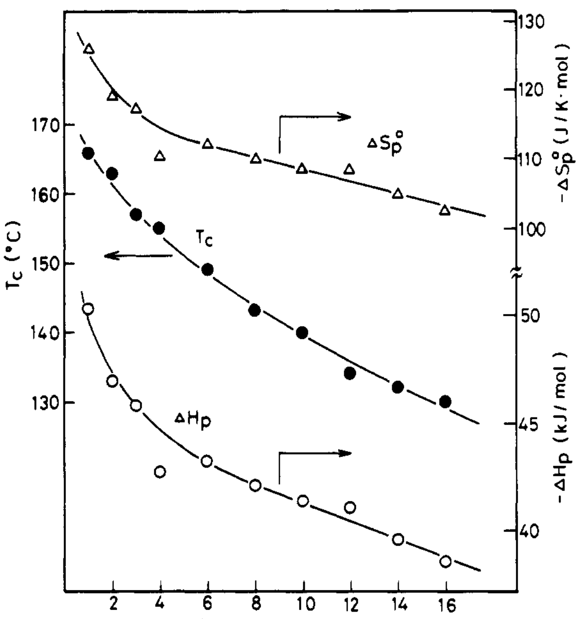


Figure 4. Relationship between the carbon numbers in the alkyl group of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines and thermodynamic parameters of polymerization: (●) T_c; (○) ΔH_p; (△) ΔS_p°.

to be 1, the ΔS_p° can be obtained by eq 2, which is derived from eq 1, where M_w is the molecular weight of the monomer.

$$\Delta S_p^\circ = \frac{\Delta H_p}{T_c} - R \ln \frac{1000s}{M_w} \qquad (2)$$

The values are given in Table I.

The thermodynamic parameters of polymerization (T_c, ΔH_p, and ΔS_p°) in Table I are plotted in Figure 4 against the carbon numbers in the alkyl group of the monomers. As shown in Figure 4, they decrease with an increase in the length of the alkyl chain. It is well-known that the ceiling temperature depends on the monomer concentration. The cause of the decrease in T_c may involve the lowering of the monomer concentration in the molten state due to the increase in the molecular weight of the monomer with the number of carbon atoms. On the other hand, the heat of polymerization is generally independent of the monomer concentration. Therefore, the decrease of ΔH_p is the effect of the alkyl chain length. This is due to the steric hindrance in the polymer side, which occurs in a less stable state with an increase in the length of the alkyl group. Because T_c generally relates to ΔH_p, the decrease of the T_c depends not only on the monomer concentration in the molten state but also on the decrease of the ΔH_p caused by the steric hindrance of the alkyl group. The ΔS_p° slightly decreases with the alkyl chain length. In general, steric hindrance in the polymer, which markedly affects ΔH_p, has comparatively little effect on ΔS_p°. For example, $-\Delta S_p^\circ$ for styrene amounted to around 105 J/K·mol, whereas the corresponding value for α-methylstyrene was found to be around 109 J/K·mol, even if the difference in the ΔH_p between two monomers was ca. 40 kJ/mol.[16] The reason why the present $-\Delta S_p^\circ$ decreased with an increase in the length of the alkyl chain might be that the rotation of the polymer chain becomes easier with an increase in the length of the alkyl group due to the increase in the space of the polymer. A similar tendency was found by Hashimoto et al.[17] in the equilibrium anionic polymerization of aliphatic aldehydes such as pentanal, hexanal, and octanal. They reported that $-\Delta S_p^\circ$ diminished with an increase of the length of the *n*-alkyl group because the mobility of the long alkyl groups increases more effectively in the polymer states rather than in the monomer states.

In Figure 2, a polymerization exotherm cannot be observed in the DSC curve for N18 and N22. Because T_c decreased with the alkyl chain length as shown in Figure 4, the lower T_c would be predictable for both monomers. Further, the initiation temperature of polymerization shifted to higher temperature with an increase in the length of the alkyl group for monomers containing above 12 carbon numbers of the alkyl group. This information suggests that T_c is reached before both the monomers can be polymerized.

Thermodynamic Parameters from Equilibrium Monomer Concentration. Because the DSC method described above is based on the dynamic equilibrium, the resulting T_c might be doubtful. In order to confirm the validity of the thermodynamic parameters obtained from the DSC technique, particularly for the T_c, these values were also obtained from the equilibrium monomer concentration determined by isothermal bulk polymerization and compared with the above values.

Since the specific gravity of the polymerization system (s) could not be estimated, a residual monomer fraction after an isothermal polymerization was used as the equilibrium monomer concentration ($[\mathrm{M}]_e$). When the unit of $[\mathrm{M}]_e$ (mol/L) is converted into a fraction (%), eq 3 is derived from eq 1. If the change in s with temperature is

$$\ln\,[\mathrm{M}]_e\,(\%) = \frac{\Delta H_p}{RT} - \frac{\Delta S_p^\circ}{R} + \ln \frac{M_w}{10s} \qquad (3)$$

negligible, the linear relationship is valid between $\ln\,[\mathrm{M}]_e$ (%) and $1/T$. For the application of above equation, thermal polymerization of N6 and N10 was carried out with DSC operated isothermally at different temperatures. The attainment of equilibrium could be read from the DSC thermograms, which was completed in 30 min in all cases. After the polymerization, the $[\mathrm{M}]_e$ (%) was determined by UV spectrometry. The $\ln\,[\mathrm{M}]_e$ (%) is plotted in Figure 5 against reciprocal polymerization tem-

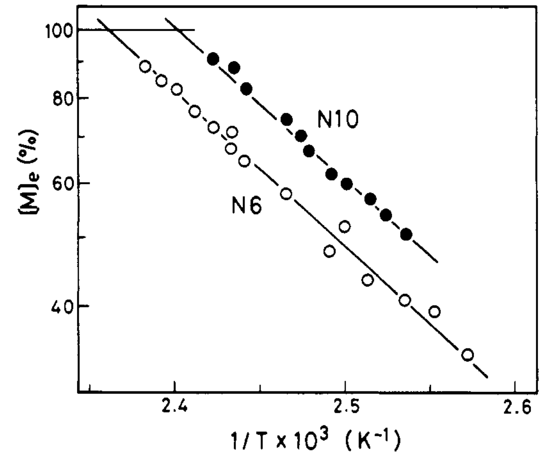


Figure 5. Logarithm of the equilibrium monomer concentration plotted against the reciprocal polymerization temperature. Monomer: (○) N6; (●) N10.

Table II
Thermodynamic Parameters of Polymerization Determined from Equilibrium Monomer Concentration

monomer	T_c, °C	$-\Delta H_p$, kJ/mol	$-\Delta S_p°$, J/K·mol
N6	150.2 ± 0.8	43.9 ± 0.8	113.4 ± 1.7
N10	141.8 ± 1.4	41.9 ± 0.7	109.3 ± 1.3

perature ($1/T$) for N6 and N10. A linear relationship was observed for both monomers. ΔH_p and T_c were obtained from the slope of the straight line and the temperature extrapolated to be $[M]_e = 100\%$, respectively. The results are shown in Table II, with the error determined by the linear regression method. The values were in good agreement with those in Table I determined by the dynamic DSC method. It is confirmed that the T_c obtained from the dynamic DSC measurement is a reasonable value, although the method is based on the dynamic equilibrium.

In conclusion, we demonstrated that the thermodynamic parameters of polymerization could be easily determined from a DSC thermogram and remarkably depended on the alkyl chain length in the monomers.

References and Notes

(1) (a) Horie, H.; Mita, I.; Kanbe, H. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2663. (b) Horie, H.; Mita, I.; Kanbe, H. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 2561.
(2) Kishore, K.; Santhanalakshmi, K. N. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2367.
(3) Kishore, K.; Santhanalakshmi, K. N. *J. Macromol. Sci. Chem.* **1981**, *A16*, 941.
(4) Kishore, K.; Santhanalakshmi, K. N. *J. Macromol. Sci. Chem.* **1983**, *A20*, 23.
(5) Malavašič, T.; Osredkar, U.; Anžur, L.; Vizovišek, I. *J. Macromol. Sci. Chem.* **1984**, *A23*, 853.
(6) Yuki, Y.; Ootani, M. *Kobunshi Kagaku* **1973**, *30*, 275.
(7) Yuki, Y.; Oouchi, T. *Kobunshi Ronbunshu* **1973**, *31*, 67.
(8) Yuki, Y.; Kunisada, H.; Seo, T.; Kakurai, T. *Kobunshi Ronbunshu* **1983**, *40*, 733.
(9) (a) Yuki, Y.; Kunisada, H. *Nippon Kagaku Kaishi* **1985**, 242. (b) Yuki, Y.; Kunisada, H.; Sakakibara, K.; Yamada, Y.; Tsutsui, F. *Nippon Kagaku Kaishi* **1985**, 1745.
(10) Yuki, Y.; Kunisada, H.; Taniuchi, J.; Takizuka, N. *Nippon Kagaku Kaishi* **1987**, 224.
(11) Kunisada, H.; Yuki, Y.; Tanaka, T. *Nippon Kagaku Kaishi* **1988**, 1868.
(12) Kunisada, H.; Yuki, Y.; Ochiai, T.; Nishii, M.; Sano, S. *Kobunshi Ronbunshu* **1988**, *45*, 911.
(13) Kunisada, H.; Yuki, Y.; Arai, H. *Nippon Kagaku Kaishi* **1989**, 97.
(14) Kunisada, H.; Yuki, Y.; Kondo, S.; Miyatake, J.; Maeda, C. *Polym. J.* **1990**, *22*, 559.
(15) Dainton, F. S.; Ivin, K. J. *Quart. Rev.* **1958**, *12*, 61.
(16) (a) Sawada, H. *J. Macromol. Sci. Rev., Macromol. Chem.* **1969**, *C3*, 313. (b) Sawada, H. *Thermodynamics of Polymerization*; Marcel Dekker: New York, 1976.
(17) Hashimoto, K.; Sumitomo, H. *Polym. J.* **1979**, *11*, 745.

Registry No. N3, 129209-46-7; N6, 129231-32-9; N8, 129209-48-9; N10, 129209-50-3; N12, 129209-52-5; N14, 129209-54-7; N16, 129209-56-9; N18, 129209-58-1; N22, 129209-60-5.