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THERMAL STUDY OF GLASS TRANSITIONS IN BINARY SYSTEMS OF SIMPLE HYDROCARBONS*

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Glass transition phenomena of four binary systems composed of simple hydrocarbons were studied by means of the differential thermal analysis (DTA). For all the systems, a definite glass transition was observed and a monotonous relation between the glass transition temperature (T_g) and composition (x) was obtained. The composition dependence of T_g was analyzed in terms of the entropy theory based on the regular solution model. The theoretical prediction could not reproduce our results other than (1-butene)$_x$(1-pentene)$_{1-x}$ system. This disagreement is considered to be due to deviations of the present systems from the regular solution, and the accompanying excess configurational entropy S_c^E was estimated as a function of composition. Extraordinarily large values of S_c^E were obtained for (propene)$_x$(propane)$_{1-x}$ and (propene)$_x$(1–pentene)$_{1-x}$ systems.

Keywords: DTA, glass transitions, hydrocarbons

Introduction

One of the most interesting subjects in solution chemistry is the dynamics of the constituent molecules, in which the intramolecular mode-mode coupling and intermolecular correlation are argued along with the local structure around each molecule. The glass transition of binary mixtures can be accounted for as the dynamical property of the molecular motions in the ultra-slow regime. From such interests, some experimental studies on the composition dependence of the glass transition temperatures have been carried out for ionic solutions [1], alcohols [2] and organic halides [3]. On the other hand, the configurational entropy is the ther-

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** Present Address: Naruto University of Education, Takashima, Naruto-cho, Naruto-shi Tokushima 772, Japan modynamic quantity related to the correlation between molecules and has been expected to play an important role in describing the kinetic properties of liquid near the glass transition temperature [4,5]. It is also an interesting problem how the entropy of mixing is included in the configurational entropy.

Based on the entropy theory, Gordon *et al.* [6] developed a phenomenological theory (GRGR theory) to reproduce the glass transition temperatures of binary systems. Their basic concept was the same as that suggested by Adam and Gibbs [5]; the glass transition is a kinetic manifestation of the underlying second order phase transition which may occur at the Kauzmann temperature T_K in an ideal equilibrium liquid. They also demonstrated that the composition dependence of the Kauzmann temperature is obtainable for the regular solution system if the temperature dependence of the configurational heat capacity is known. By assuming that the temperature dependence of the configurational heat capacity is proportional to $1/T$, the composition dependence of the Kauzmann temperature T_K is given by

$$T_K(x) = \frac{xT_{K1} + C(1-x)T_{K2}}{x + C(1-x)} \tag{1}$$

where x, T_{K1} and T_{K2} denote the mole fraction of component 1 and the Kauzmann temperatures of component 1 and 2, respectively. The parameter C is a constant which can be obtained from the heat capacity jumps of pure components at T_K. This is the same functional form as an empirical relation for the glass transition temperature T_g [6].

$$T_g(x) = \frac{xT_{g1} + C(1-x)T_{g2}}{x + C(1-x)} \tag{2}$$

Gordon *et al.* assumed that the composition dependence of both T_K and T_g can be reproduced by the same functional form with a common parameter C. Though this assumption has not been confirmed theoretically, the GRGR theory is interesting in the sense that it provides the composition dependence of T_g of binary system only from the thermodynamic quantities of pure components with no adjustable parameter.

In this study, the glass transition phenomena of four binary systems of simple *n*-alkanes and 1-alkenes were investigated by means of DTA experiment. Compared with the binary systems studied so far, the present systems consist of components with a simple intermolecular interaction which is dominated by the dispersion force. The purpose of the present study is to understand the composition dependence of the glass transition temperature from the standpoint of entropy theory. The GRGR theory was applied to our data, and the deviation from the regular solution model was examined. The excess configurational entropy, which is the measure of the deviation, was evaluated as a function of the composition.

Entropy theory of binary glass

For the pure substances, the configurational entropy, S_c at a given temperature T can be evaluated from

$$S_c(T) = \Delta_{fus}S - \int_T^{T_{fus}} \frac{C_p^{liq} - C_p^{cry}}{T'} dT', \tag{3}$$

where $\Delta_{fus}S$ is the entropy of fusion, and C_p^{liq} and C_p^{cry} are the heat capacities of liquid and crystal, respectively. Since the Kauzmann temperature T_K is the temperature at which the configurational entropy vanishes, the T_K can be evaluated by use of the relation

$$\Delta_{fus}S = \int_T^{T_{fus}} \frac{C_p^{liq} - C_p^{cry}}{T'} dT'. \tag{4}$$

For the mixture, however, heat capacity data have seldom been measured so that the T_K value is approximately estimated by means of the heat capacity data of pure substances as follows.

In general, the entropy of mixing $\Delta_{mix}S$ of the real solution is given by

$$\Delta_{mix}S = -R[x\ln x + (1-x)\ln(1-x)] + \Delta_{mix}S^E, \tag{5}$$

where the last term is the excess entropy of mixing. This term is assumed to be zero at any temperature for regular solutions.

On evaluating the configurational entropy of binary system, the solid solution should be taken as the reference state in which no configurational disorder remains. The entropies of liquid solution (ls) and solid solution (ss) are given by

$$S^{ls}(x,T) = xS_1^{liq}(T) + (1-x)S_2^{liq}(T) - R[x\ln x + (1-x)\ln(1-x)] + \Delta_{mix}S^{E,ls}(x,T), \tag{6}$$

and

$$S^{ss}(x,T) = xS_1^{cry}(T) + (1-x)S_2^{cry}(T) - R[x\ln x + (1-x)\ln(1-x)] + \Delta_{mix}S^{E,ss}(x,T), \tag{7}$$

respectively. Here, S_i^{α} represents the entropy of the i-th pure component in the phase α. Subtraction of Eq. (7) from (6) gives

$$S_c(x,T) = xS_{c1}(T) + (1-x)S_{c2}(T) + S_c^E(x,T), \tag{8}$$

where S_c (x, T) is the excess configurational entropy defined as

$$S_c^E(x,T)=\Delta_{mix}S^{E,ls}(x,T)-\Delta_{mix}S^{E,ss}(x,T)\,, \tag{9}$$

It is clear that this term also becomes zero for regular solutions.

For the regular solution, T_K can be evaluated from Eq. (8) and a basic condition

$$S_c(x, T_K)=0. \tag{10}$$

Here, S_{c1} (T) and S_{c2} (T) can be evaluated from the heat capacity data of each pure component by using Eq. (3) without any adjustable parameter. For the real solution systems, however, the evaluation of $S_c^E(x, T)$, which is generally very difficult, is required to determine T_K. A non-zero value for S_c^E means that the mixing induces some changes in the number of configurational states. In such cases, it is necessary to take S_c^E into account for the determination of T_K by using Eq. (8).

Experimental

The commercial materials of propane (Gasukuro Kogyo Inc.; 99.5%), propene (Gasukuro Kogyo Inc.; 99.5%), 1-butene (Tokyo Kasei Kogyo Co. Ltd.; 98.5%) and 1-pentene (Tokyo Kasei Kogyo Co. Ltd.; 98.5%) were used without further purification. Four binary mixtures of propene-propane, propene-1-butene, propene-1-pentene and 1-butene-1-pentene systems were prepared. Preparation of a mixture was done in the same way as described elsewhere [7]. The composition of a sample mixture was determined as follows. A specified volume of a hand-made Pyrex vacuum-line was filled with the vapor of the first component at a known pressure.

The vapor was collected into a sample container with a polytetrafluoroethylene (PTFE) cock, or a DTA tube. The second component vapor in the same space was also collected in the same manner. The composition of the mixture is estimated as the ratio of the pressures of the two components, neglecting small correction of their virial coefficients. Two DTA apparatuses were used in the present study. One is an apparatus developed for the vapor-deposited samples which realized the sample deposition at liquid helium temperature (type I apparatus). Three systems but for 1-butene-1-pentene were measured by the type I apparatus. The system of 1-butene-1-pentene was measured by a conventional type of DTA apparatus which is workable down to the liquid hydrogen temperature (type II apparatus). The details of each apparatus were described elsewhere [8, 9].

Typical experimental DTA curves (for 1-butene) obtained by both apparatuses are given in Fig. 1. The heating rates of DTA experiments were around 2 $K\cdot min^{-1}$

and 1 K·min^{-1} in the type I and type II apparatuses, respectively. A glass transition can be recognized as a definite jump of the DTA curve. The glass transition temperature was determined as an intersection of the extrapolations of the base-line and the rising part of the base-line shift. The precision of the determined temperature was within ± 0.3 K. Both the non-crystalline samples gave the same T_g values, irrespectively of the vitrification processes.

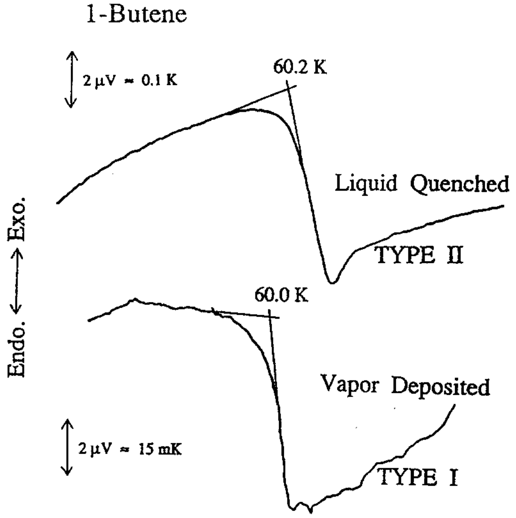

Fig. 1 Practical DTA curves of 1-butene around the glass transition point

Results and discussion

Results of DTA experiment

Figures 2 to 5 show the schematic drawings of the DTA curves. For all the samples, a step-like anomaly due to the glass transition was observed. The determined glass transition temperatures were shown in each figure.

In the cases of the pure propene and the propene-propane system, some exothermic peaks were observed following to the glass transition. These effects are due to the irreversible crystallization and stabilizations from an unidentified metastable to the stable crystal. The endothermic peak observed in the higher temperature region is due to the fusion process. The fusion for $x = 0.25$ was clearly split into a sharp and a broad peaks. This type of fusion phenomenon is typically observed for systems exhibiting a eutectic melting. In the present system, the phase separation could take place on crystallization. No indications of the eutectic melting for the $x = 0.5$ and 0.75 samples are probably due to the fact that temperature difference between the eutectic point and the liquidus line is too small to be detected separately by DTA.

The glass transition temperatures of the four systems were plotted against the mole fraction in Figs 6 to 9. In all the systems, T_g changed monotonously against

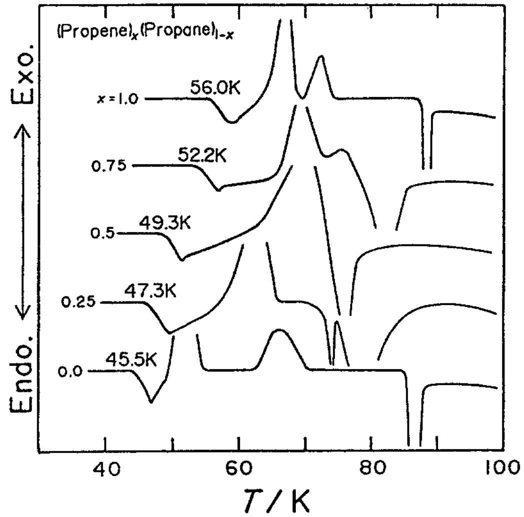

Fig. 2 Schematic drawings of DTA curves of vapor-deposited (propene)$_x$(propane)$_{1-x}$ system

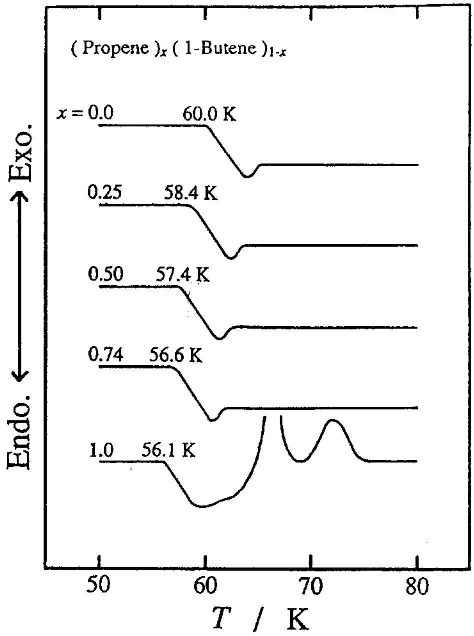

Fig. 3 Schematic drawings of DTA curves of vapor-deposited (propene)$_x$(1–butene)$_{1-x}$ system

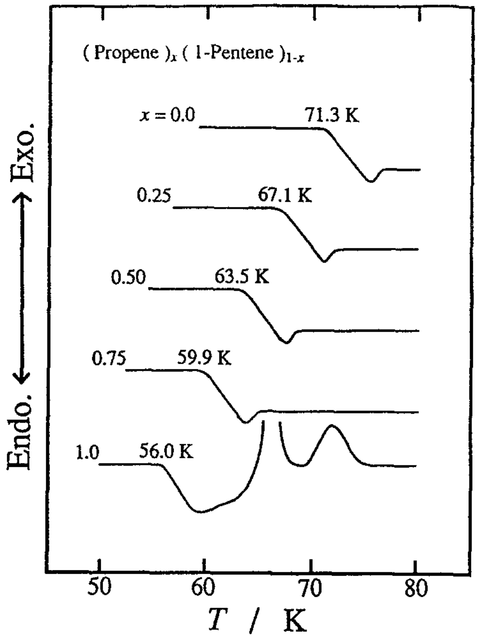

Fig. 4 Schematic drawings of DTA curves of vapor-deposited (propene)$_x$(1–pentene)$_{1-x}$ system

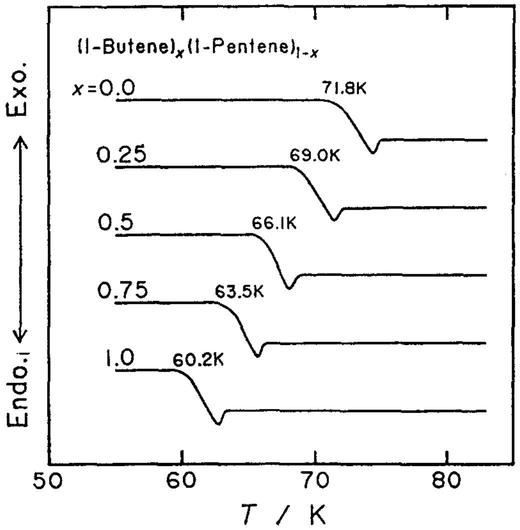

Fig. 5 Schematic drawings of DTA curves of liquid-quenched (1–butene)$_x$(1–pentene)$_{1-x}$ system

Table 1 Determined parameter C of Eqs (1) and (2). C_{exp} is obtained by fitting $T_g(x)$ to Eq. (2), and C_{theory} by fitting $T_K(x)$ to Eq. (1)

System	C_{exp}	C_{theory}
(propene)$_x$(propane)$_{1-x}$	1.71	0.976
(propene)$_x$(1–butene)$_{1-x}$	0.472	1.30
(propene)$_x$(1–pentene)$_{1-x}$	1.03	1.40
(1–butene)$_x$(1–pentene)$_{1-x}$	1.04	1.08

the composition. The solid lines are the calculated curves of T_g best fitted to Eq. (2). Values of the parameter C determined by the least squares method are shown in Table 1.

Analysis in terms of the regular solution model

The configurational entropies of the pure substances were evaluated from the data of the heat capacity and entropy of fusion by using Eq. (3). The extrapolations of the heat capacities of the equilibrium liquids and crystals were carried out by the least squares fitting of the data to power polynomical functions. The determined coefficients of the polynominals are tabulated in Table 2 along with the literature sources of the heat capacity data. The composition dependence of T_K was evaluated for every 10 mole% of composition. The T_K data were fitted to Eq. (1) by the least squares method and the obtained parameters C were tabulated as C_{theory} in Table 1.

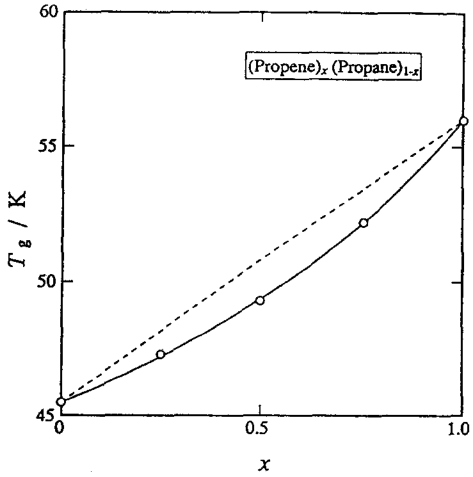

Fig. 6 Composition dependence of the glass transition temperature of (propene)$_x$(propane)$_{1-x}$ system. The solid curve is best-fitted to Eq. (2) and the dashed one from the GRGR theory (see the text for details)

The broken curves drawn in Figs 6 to 9 are the T_g curves reproduced by using Eq. (2) along with the best-fit value of the parameter C obtained for T_K. For the system of (1-butene)$_x$(1-pentene)$_{1-x}$, the calculated T_g curve gives a good agreement with the experimental data. On the other hand, definite deviations were found for other systems. These deviations indicate the invalidity of the GRGR model for the present systems.

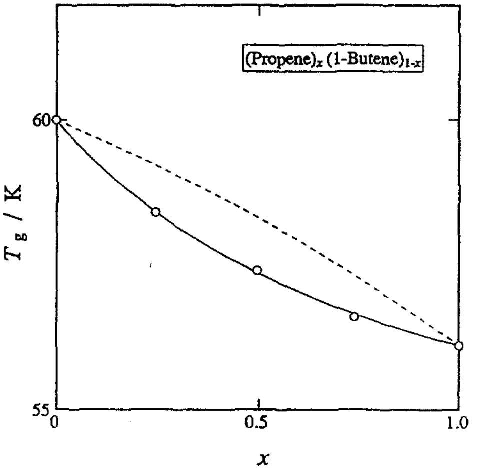

Fig. 7 Composition dependence of the glass transition temperature of (propene)$_x$(1-butene)$_{1-x}$ system. The solid curve is best fitted to Eq. (2) and the dashed one from the GRGR theory (see the text for details)

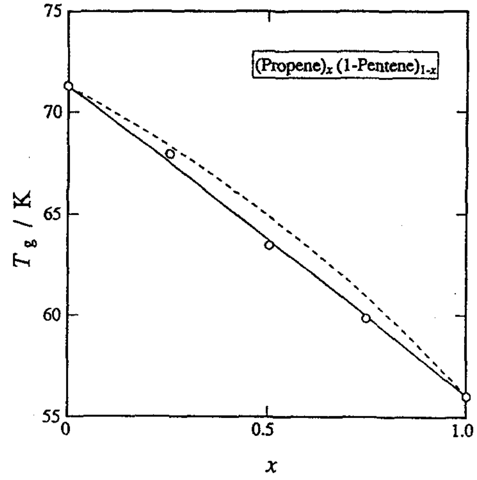

Fig. 8 Composition dependence of the glass transition temperature of (propene)$_x$(1–pentene)$_{1-x}$ system. The solid curve is best-fitted to Eq. (2) and the dashed one from the GRGR theory (see the text for details)

Table 2 Coefficients of power series used in the evaluation of T_K. The heat capacity was expressed in the form $C_p / \mathrm{J\cdot K^{-1}\,mol^{-1}} = \sum_{i=0}^{N} C(i)\, T_s^{i}$ i with $T_s = [(T/\mathrm{K}) - A]/B$

	Propane[1)]		Propene[2)]		1–Butene[3)]		1–Pentene[4)]	
	Crystal	Liquid	Crystal	Liquid	Crystal	Liquid	Crystal	Liquid
A	49.145	159.835	47.09	155.625	0	0	57.6693	110.556
B	39.8389	77.9611	36.5667	75.3056	1	1	35.17	42.8209
$C(0)$	32.0852	88.902	34.0905	86.9944	–16.9669	149.57	47.5104	129.286
$C(1)$	28.1879	7.44781	24.3353	–0.437641	1.38017	–0.754388	26.3881	–3.15769
$C(2)$	–10.7918	3.08457	–9.58306	6.53027	$-6.2018\cdot 10^{-3}$	$3.35523\cdot 10^{-3}$	–6.8633	3.3751
$C(3)$	6.66491		10.1325				1.27984	–0.655784
$C(4)$	6.24419		4.15262					
$C(5)$	–8.1775		–8.30198					

A and *B* are parameters which minimize a possible error in the calculation

Source of the heat capacity data were Refs [1)] 10, [2)] 11, [3)] 12 and [4)] 13, respectively

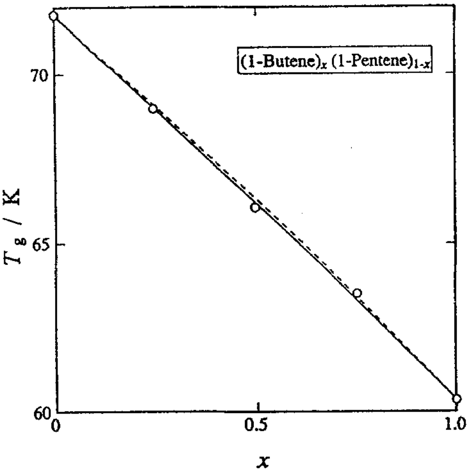

Fig. 9 Composition dependence of the glass transition temperature of (1-butene)$_x$(1-pentene)$_{1-x}$ system. The solid curve is best-fitted to Eq. (2) and the dashed one from the GRGR theory (see the text for details)

Estimation of excess configurational entropy

In the previous section, both the liquid and solid solutions are treated as regular solutions according to the GRGR theory. The disagreement between the theoretical and experimental results can be explained phenomenologically by assuming finite value of excess configurational entropy.

Inverse operations to obtain T_K and S_c^E from the experimental T_g data were tried as follows. The composition dependence of T_K was estimated by using Eq. (1) and the parameter C which is determined from the composition dependence of T_g, S_c^E at each composition is then evaluated by using Eqs (3), (8) and (10). Practically, this quantity can be evaluated as a minus value of residual configurational entropy at T_K obtained by the regular solution model. Here, we assume that S_c^E is independent of temperature.

In Fig. 10, the excess configurational entropies thus calculated are shown as a function of the composition. The error of S_c^E value is estimated to be about ±0.5 $\mathrm{J{\cdot}K^{-1}mol^{-1}}$ in the intermediate composition range. This error arises mainly from the inaccuracy inherent in the extrapolation of the liquid heat capacity towards T_K. The S_c^E values of the (1-butene)$_x$(1-pentene)$_{1-x}$ and (propene)$_x$(1–butene)$_{1-x}$ systems were zero within the error of the estimation. However, the S_c^E values beyond the error were found for other two systems. Especially for (propene)$_x$(propane)$_{1-x}$ system, the maximum value of S_c^E exceeds one third of the ideal mixing entropy of R ln2 (= 5.76 $\mathrm{J{\cdot}K^{-1}mol^{-1}}$).

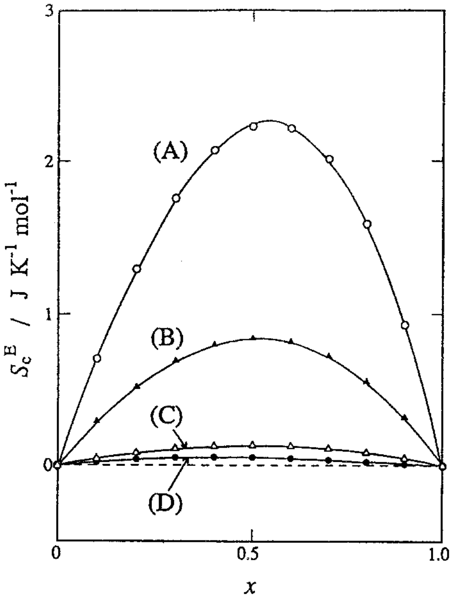

Fig. 10 Estimated excess configurational entropy S_c^E (A): (propene)$_x$(propane)$_{1-x}$, (B): (propene)$_x$(1–pentene)$_{1-x}$, (C): (1-butene)$_x$(1-pentene)$_{1-x}$, (D): (propene)$_x$(1–butene)$_{1-x}$

There are few data concerning S_c^E in literature. The value can be obtained in principle from the data of $\Delta_{mix}S^{E,ls}(x, T)$ and $\Delta_{mix}S^{E,ss}(x, T)$ by using Eq. (9). The former is easily obtained from the measurements of enthalpy of mixing and vapor pressure of the mixture in the interested temperature range. On the other hand, the latter quantity is difficult to measure because the direct mixing process cannot be realized in the solid state. Also formation of uniform solid solution is highly limited by several factors including molecular size and crystallographic symmetry of each component [16]. Most of the liquid solutions exhibit phase separation on solidification. Under such circumstances, the most useful data to be compared with our S_c^E data are $\Delta_{mix}S^{E,ls}$ of some related binary systems tabulated in Table 3. Here, the quantity $\Delta_{mix}S^{E,ss}(x, T)$ was neglected. The comparison was made at the mole fraction $x = 0.5$. Obviously, the present S_c^E values are much larger than the literature values of $\Delta_{mix}S^{E,ls}(x, T)$ beyond the possible effects of the unobtainable $\Delta_{mix}S^{E,ss}(x, T)$ value. This means that the present systems possess larger excess configurational entropy than the literature systems.

One idea to explain these unexpectedly large S_c^E in the present system is to consider the effect of temperature; i.e., in the undercooled liquid at low temperature, the correlation between the molecules is increased and so the configuration-

Table 3 Comparison of estimated excess configurational entropy with the excess entropy of mixing in related systems

Mixture	S_c^E / J·K^{-1}mol^{-1}	$\Delta_{mix}S^{E,s}$ / J·K^{-1} mol^{-1}	T / K
This work			
(propene)$_{0.5}$(propane)$_{0.5}$	2.2		
(propene)$_{0.5}$(1-butene)$_{0.5}$	0.05		
(propene)$_{0.5}$(1-pentene)$_{0.5}$	0.84		
(1-butene)$_{0.5}$(1-pentene)$_{0.5}$	0.13		
Literature			
(n-hexane)$_{0.5}$(n-decane)$_{0.5}$$^{1)}$		0.077 0.056	298.14 308.15
(ethane)$_{0.5}$(propane)$_{0.5}$$^{2)}$		0.099 0.032	112.0 255.4

Literature values are from $^{1)}$ Ref. 14 and $^{2)}$ Ref. 15

al entropy S_c of the system could change significantly by introducing the second component. Actually, the excess entropy of the (ethane)$_{0.5}$(propane)$_{0.5}$ system at 112 K is three times larger than the value at 255.4 K though all of the excess entropy cannot be attributed to the configurational part [15]. It is desired to make a direct measurement of the excess entropy at low temperatures. It is also possible to explain the large S_c^E value by the invalidity of the assumptions involved in the GRGR theory; e.g., the composition dependence of T_g and T_K can be expressed with the common value of the parameter C in Eqs (1) and (2). It is also an important subject in the future to confirm the validity of the GRGR theory further by both theoretical and experimental approaches.

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Zusammenfassung — Mittels DTA wurden Glasumwandlungserscheinungen von vier binären Systemen aus einfachen Kohlenwasserstoffen untersucht. Für alle Systeme wurde eine definitive Glasumwandlung beobachtet, wobei man eine monotone Beziehung zwischen der Glasumwandlungstemperatur (T_g) und der Zusammensetzung (x) erhielt. Die Konzentrationsabhängigkeit von T_g wurde hinsichtlich der Entropietheorie auf der Grundlage des regulären Lösungsmodelles analysiert. Die Prognose konnte die Resultate nicht reproduzieren, nur das System (1-Buten)$_x$(1-Penten)$_{1-x}$. Diese Diskrepanz wird mit der Abweichung der Systeme von einer regulären Lösung erklärt und die zusätzliche Konfigurationsentropie S_c^E wurde als Funktion der Konzentration geschätzt. Außerordentlich hohe Werte für S_c^E wurden bei den Systemen (Propen)$_x$(Propan)$_{1-x}$ und (Propen)$_x$(Penten)$_{1-x}$ erhalten.