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The Radical Polymerization and Copolymerization of Triallylidene Sorbitol with Styrene or Acrylonitrile

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The polymerization of triallylidene sorbitol (TAS) and the copolymerization of TAS with styrene (St) or acrylonitrile (AN) have been carried out, using benzoyl peroxide as an initiator at 80°C. They were kinetically investigated in relation to the degradative or effective chain transfer by the allylidene group, and by the cyclization by three double bonds. The results can be summarized as follows: 1) the relation among the rate of polymerization, R_p, the initiator concentration, (I), and the monomer concentration, (M), can be expressed by the following equation: $((\mathrm{I})/R_p-a)^{-1}=\mathrm{A}(\mathrm{M})+\mathrm{B}$, where a, A, and B are constant; 2) the ratio of the rate of unimolecular cyclization to the total rate of bimolecular propagation and the chain transfer of uncyclized radical was estimated to be 0.291; 3) the degree of polymerization depends on the monomer concentration, but not on the initiator concentration; 4) the rates of copolymerization decrease markedly with an increase in the TAS or tricrotylidene sorbitol (TCS) mole fraction in monomer mixtures; and 5) the following monomer reactivity ratios were ascertained: St(M_1)-TAS(M_2) $r_1=4.60$, $r_2=0.13$, AN(M_1)-TAS(M_2) $r_1=0.70$, $r_2=0.26$, St(M_1)-TCS(M_2) $r_1=2.31$, $r_2=0.39$, AN(M_1)-TCS(M_2) $r_1=0.30$, $r_2=0.36$. The Q and e values for the functional group were calculated from the above values as 0.05 and -0.08 (TAS), and 0.10 and -0.25 (TCS) respectively.

In a previous paper,[1] the polymerization of diallylidene pentaerythritol (DAPE) was kinetically investigated in relation to the degradative or effective chain transfer by the allylidene group, and by the cyclization by two double bonds in DAPE. The monomer reactivities have also been reported in the copolymerizations of DAPE or dicrotyridene pentaerythritol (DCPE) with various monomers.[2,3]

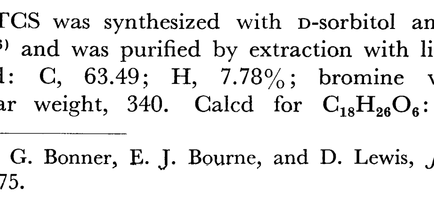
The present paper will deal with the polymerization of triallylidene sorbitol (TAS), and the difference between triallylidene and diallylidene cyclic acetal compounds will be kinetically discussed.

The copolymeizations of TAS and triallylidene pentaerythritol (TCS) with styrene (St) or acrylonitrile (AN) were carried out; they will be discussed by using the Gibbs equation.[4]

Experimental

Monomers. The TAS was prepared from D-sorbitol and acrolein by the procedure of Fisher and Smith;[5] bp 194—196°C/8 mmHg (lit,[5] bp 149—151°C/0.9 mmHg).

Found: C, 60.82; H, 6.88%; bromine value, 159; molecular weight, 296. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80%; bromine value, 161; molecular weight, 296.



TAS

The TCS was synthesized with D-sorbitol and crotonaldehyde,[6] and was purified by extraction with light oil.

Found: C, 63.49; H, 7.78%; bromine value, 140; molecular weight, 340. Calcd for $C_{18}H_{26}O_6$: C, 63.89,

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[1] T. Ouchi and M. Oiwa, *Kogyo Kagaku Zasshi*, **72**, 746 (1969).

[2] T. Ouchi, S. Yamamoto, Y. Akao, Y. Nagaoka, and M. Oiwa, *ibid.*, **71**, 1078 (1968).

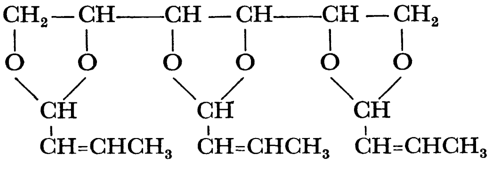
[3] T. Ouchi, S. Tatsuno, T. Nakayama, and M. Oiwa, *ibid.*, **73**, 607 (1970).

[4] W. E. Gibbs, *J. Polym. Sci.*, **A-2**, 4809 (1964).

[5] R. F. Fisher and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960).

[6] T. G. Bonner, E. J. Bourne, and D. Lewis, *J. Chem. Soc.*, **1963**, 3375.

H, 7.75%; bromine value, 140; molecular weight, 338.


TCS

The St, AN, benzoyl peroxide (BPO), benzene, and dimethylformamide (DMF) were purified by the usual methods.

Polymerization Procedure. The polymerization was carried out using BPO as a radical initiator. Measured amounts of each monomer, initiator, and solvent were placed in an ampoule, which was then degassed twice in the usual manner and flushed with nitrogen. The ampoule was sealed under a vacuum and then set into a thermostat. After a definite reaction time, the ampoule was removed from the thermostat; the polymer was then separated by pouring the contents into a large amount of petroleum ether, followed by centrifuging.

The polymer thus obtained was then washed repeatedly with petroleum ether and dried *in vacuo* to a constant weight. The conversion of the polymer was less than 10%.

Analyses of the Polymer. The composition of the copolymer was determined by elementary analysis. The residual unsaturation of the polymer was calculated from the composition and the bromine value (BV) obtained by the bromite-bromate method.[7] The molecular weight of the polymer was measured with a vapor-pressure osmometer (Hewlett Packard Model-302), using benzene as the solvent at 37°C.

Kinetics of Homopolymerization

The initial polymerization of triallylidene cyclic acetal compounds is treated in a manner similar to that described in previous papers,[1,8] including the chain transfer and the cyclization. The kinetic equations are derived by assuming the following elementary reactions:

Decomposition of initiator	$I \rightarrow 2R\cdot$	$2k_d(I)$
Initiation	$R\cdot + M \rightarrow M\cdot$	$3k_i(R\cdot)(M)$
Cyclization	$M\cdot \rightarrow M_c\cdot$	$k_c(M\cdot)$
Propagation	$M\cdot + M \rightarrow M\cdot$	$3k_p(M\cdot)(M)$
	$M_c\cdot + M \rightarrow M\cdot$	$3k_{cp}(M_c\cdot)(M)$
Effective chain transfer	$R\cdot + M \rightarrow R' + M\cdot$	$3k_i'(R\cdot)(M)$
	$M\cdot + M \rightarrow P + M\cdot$	$3k_{tr}(M\cdot)(M)$
	$M_c\cdot + M \rightarrow P + M\cdot$	$3k_{ct}(M_c\cdot)(M)$
Degradative chain transfer	$R\cdot + M \rightarrow R' + M^*$	$3k_i^*(R\cdot)(M)$
	$M\cdot + M \rightarrow P + M^*$	$3k_{tr}^*(M\cdot)(M)$
	$M_c\cdot + M \rightarrow P + M^*$	$3k_{ct}^*(M_c\cdot)(M)$

where I denotes an initiator; R·, an initiator radical; M, a monomer; M· the uncyclized radical; $M_c\cdot$, the cyclized radical; R′, the inactive product; M*, the stable radical, and P, a polymer.

The following equations can be obtained by assuming steady-state conditions.

The rate of polymerization, R_p, is given by:

$$R_p = \left(\frac{3(M) + c}{3a(M) + bc}\right)(I) \tag{1}$$

which, on rearrangement, gives:

$$(3(M) + c)(I)/R_p = 3a(M) + bc \tag{2}$$

$$\frac{1}{(I)/R_p - a} = \left(\frac{3}{b - a}\right)\left(\frac{(M)}{c} + \frac{1}{3}\right) \tag{3}$$

The residual unsaturation of the polymer, $3R_{us}$, is shown by:

$$\frac{1}{3R_{us}} - 1 = \frac{c}{3(M)} \tag{4}$$

The relation among the degree of polymerization, $\bar{P}_n$, and the monomer and initiator concentrations is represented by:

$$\frac{R_p(3a(M) + bc}{\bar{P}_n(I)} = 6a\gamma_i(k_i' + k_d/\gamma_i + k_{tr}/k_{tr})^*(M) \tag{5}$$

$$+ 3ab\gamma_i(k_i' + k_d/\gamma_i + k_{ct}/k_{ct}^*)$$

where:

$$\gamma_i = k_d(k_i + k_i')/(k_i + k_i' + k_i^*)$$

$$a_{tr}^* = k_{tr}^*/(k_p + k_{tr} + k_{tr}^*)$$

$$b_{ct}^* = k_{ct}^*/(k_{cp} + k_{ct} + k_{ct}^*)$$

$$a = a_{tr}^*/2\gamma_i,\ b = b_{ct}^*/2\gamma_i$$

$$c = k_c/(k_p + k_{tr} + k_{tr}^*)$$

Results and Discussion

Polymerization of TAS. The polymerization of TAS was investigated under different initiator and monomer concentrations at 80°C. The results are given in Table 1, in which the values of the residual unsaturation and the molecular weight are estimated by extrapolating to zero for conversion.

The Residual Unsaturation. As can be seen from Table 1, the residual unsaturation is independent of the initiator concentration, but decreases with a decrease in the monomer concentration.

The plots of $(1/3R_{us}$—1) against 1/(M) are shown in Fig. 1. A straight line through the point of origin was obtained, as predicted by Eq. (4). By using this slope, *c* was obtained as 0.873 mol/*l*.

The Rate of Polymerization. When the monomer concentration is kept constant and the initiator concentration is varied, it may be expected from Eq. (1) that R_p will give a straight line with (I). The result is shown in Fig. 2, in which the experimental data are very close to the calculated linear relationship.

By using the *c* value thus obtained, the *a* and *b* values were calculated by applying the method of least-squares to Eq. (2); *a* and *b* were 4.73×10^3 sec and 9.73×10^4 sec respectively (Fig. 3).

By using the *a* value thus obtained the plots of $((I)/R_p—a)^{-1}$ against (M) according Eq. (3) shown in Fig. 4 were obtained; they show a good linear relationship. Therefore, the *a* value seems to be proper.

The Degree of Polymerization. As can be seen in Table 1, the degree of polymerization, $\bar{P}_n$, is very small;

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[7] I. P. Losev and O. Y. Fedotoba, "Praktikum po Khimii Vysokopolimernykh Soedinenii," Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatelstvo Khimicheskoi Literatury, Moskova.

[8] T. Ouchi, S. Tatsuno, T. Nakayama, and M. Oiwa, This Bulletin, **43**, 2241 (1970).

Table 1. Polymerization of TAS at 80°C

(BPO) $(\times 10^{-1}$ mol/$l)$	(TAS) (mol/l)	R_p $(\times 10^{-6}$ mol/$l\cdot$sec)	BV	$3R_{us}$	Molecular weight
3.30	1.35	19.5	88.0	0.816	859
2.48	1.35	15.0	88.9	0.824	804
1.65	1.35	7.80	88.5	0.820	850
0.826	1.35	5.63	87.9	0.815	827
1.65	0.676	5.04	75.2	0.697	837
1.65	0.542	4.49	70.5	0.653	813
1.65	0.452	4.03	67.0	0.621	808

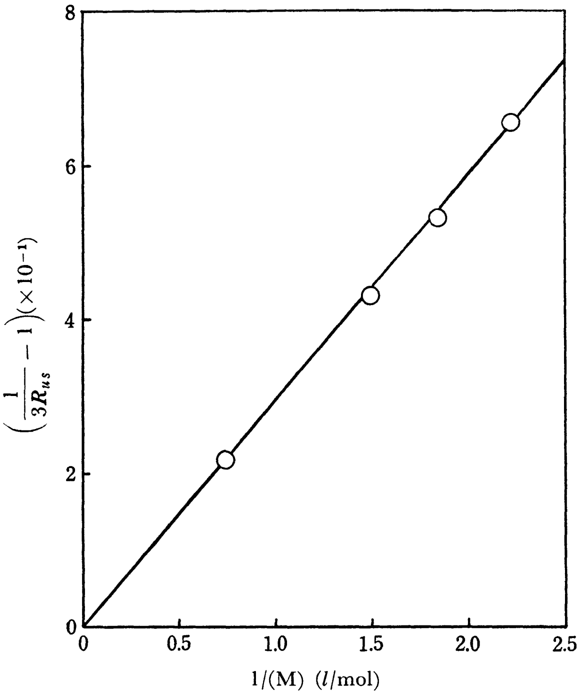

Fig. 1. Plots of $(1/3R_{us}-1)$ vs. 1/(M).

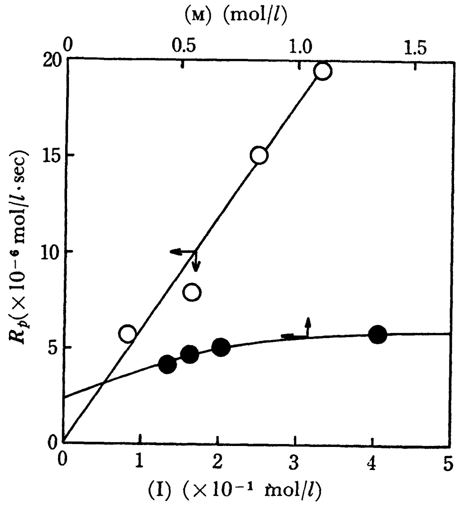

Fig. 2. Plots of rate of polymerization against the initiator and monomer concentrations.

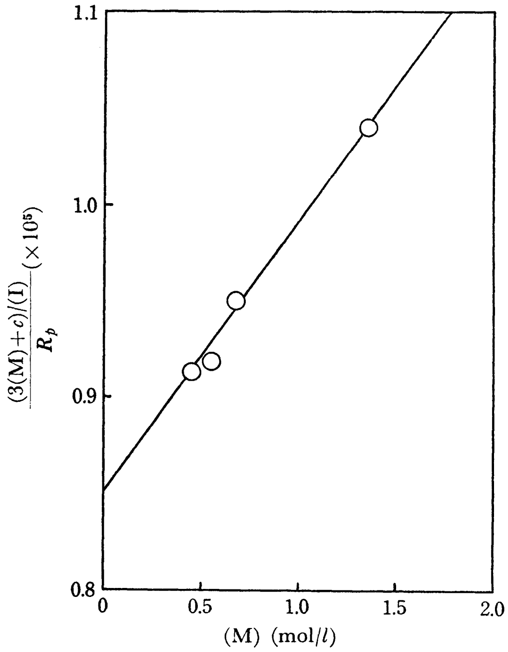

Fig. 3. Plots of $\frac{(3(\mathrm{M})+c)/(\mathrm{I})}{R_p}$ vs. (M).

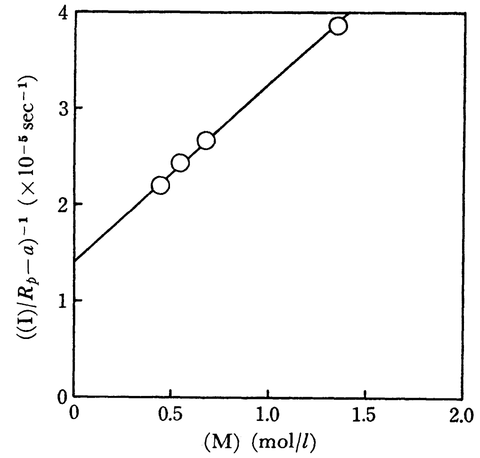

Fig. 4. Plots of $((\mathrm{I})R_p-a)^{-1}$ vs. (M).

it is independent of the initiator concentration, but increases with an increase in the monomer concentration. A similar tendency has been found on the polymerization of DAPE.[1] The plots of $R_p/\bar{P}_n$ against (I) and $(3a(\mathrm{M})+bc)R_p/\bar{P}_n(\mathrm{I})$ against (M) are shown in Fig. 5; they have a good linear relationship and satisfy Eq. (5). Accordingly, these results suggest that the a, b, and c values obtained here are justifiable on the polymerization of TAS.

Generally, k_d is of the order of about 10^{-5}—10^{-6} in

Table 2. Polymerization of parameters

Monomer	a ($\times 10^3$ sec)	b ($\times 10^4$ sec)	$\frac{k_c}{3(k_p+k_{tr}+k_{tr}^*)}$ (M)	$\frac{k_c}{2(k_p+k_{tr}+k_{tr}^*)}$ (M)
TAS	4.73	9.73	0.291	—
DAPE	2.00	2.00	—	0.276

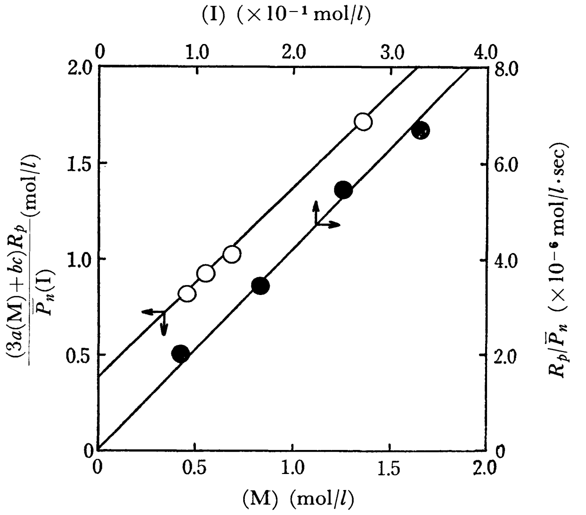

Fig. 5. Plots of $(3a(\mathrm{M})+bc)R_p/\bar{P}_n(\mathrm{I})$ *vs.* (M) and $R_p/\bar{P}_n$ *vs.* (I).

the case of a radical polymerization, as is well known.[9] Consequently, a_{tr}^* and b_{tr}^* were estimated to be of the order of about 10^{-2}—10^{-3} and 10^{-1}—10^{-2}; the degradative chain transfer may preferentially occur rather than the propagation.

Comparison of Parameters. The polymerization parameters for TAS and DAPE are summarized in Table 2.

It was found that the a and b of TAS were larger than those of DAPE. Consequently, the degradative chain transfer is found to occur more readily on TAS than on DAPE. This may result from the difference in the probablity of collision between diallylidene and triallylidene compounds.

On the other hand, the ratios of the rate of cyclization to the total rates of propagation and chain transfer for TAS polymerization were larger than those for DAPE; triallylidene compounds were cyclized more easily than diallylidene compounds. The difference in steric hindrance between tri- and diallylidene cyclic acetals may cause such tendency.

For investigating the effect of the temperature on polymerization, the polymerization was carried out at 60, 70, and 80°C. The overall activation energy, as calculated from the Arrhenius plot, was 17.3 kcal/mol, which was nearly equal to that of the usual radical polymerization.

Copolymerization. The dependence of the monomer composition on the rate of copolymerization at 80°C is shown in Fig. 6. The rates of copolymerization decrease markedly with an increase in the mole fraction of TAS in the monomer mixtures. This tendency may be ascribed to the degradative chain transfer by the allylidene group and to the steric hindrance by the cyclic acetal.

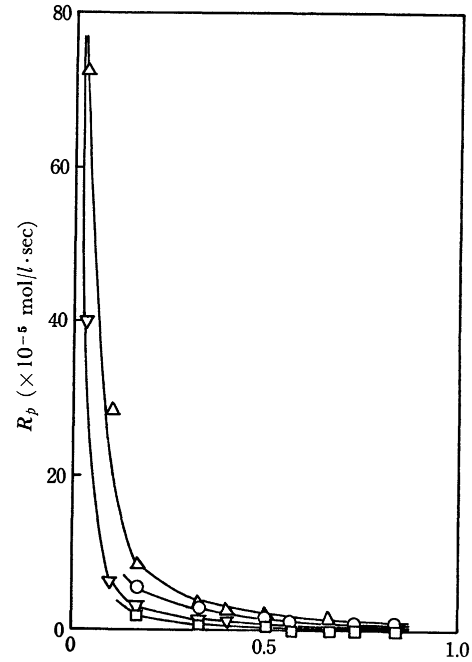

Fig. 6. Plots of the rate of copolymerization against the monomer composition at 60°C.
○: St-TAS, △: AN-TAS, □: St-TCS, ▽: AN-TCS

Monomer Reactivity Ratios. Figure 7 shows the polymer composition as a function of the monomer composition. Figure 8 shows the residual unsaturation as a function of the copolymer composition. These results mean that the residual unsaturations of the copolymers obtained decreased slightly with an increase in the TAS or TCS, and were nearly equal to 1.0. Accordingly, the cyclization may be approximately negligible on these systems of copolymerization.

The functional group reactivity ratios, r_1' and r_2', determined according to a modification of the Gibbs copolymerization equation,[4] are summarized in Table 3.

In Fig. 7 the theoretical solid curves calculated from the resulting reactivity ratios are shown to agree very closely with the experimental measurements.

The Q' and e' values for TAS and TCS, as calculated from the r_1' and r_2' values, are shown in Table 3.

The average values of Q' and e' for TAS, TCS, DAPE, and DCPE were estimated to be as follows: TAS $Q'=0.05$, $e'=-0.08$; TCS $Q'=0.10$, $e'=-0.25$; DAPE $Q'=0.03$,[2] $e'=0.0$;[2] DCPE $Q'=0.01$,[3] $e'=-0.32$.[3]

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[9] J. Brandrup and H. E. Immergut, "Polymer Handbook," John Wiley & Sons, New York (1965).

[10] G. E. Ham, "Copolymerization," Intersci. Pub., New York (1964), p. 845.

Table 3. Reactivity ratios for TAS or TCS(M_2)-monovinyl compounds (M_1) systems

M_1	M_2	Monomer		Functional group		Q_1[10]	e_1[10]	Q_2'	e_2'
		r_1	r_2	r_1'*	r_2'*				
St	TAS	4.60	0.13	13.8	0.04_3	1.00	−0.80	0.04	−0.06
AN	TAS	0.70	0.26	2.10	0.08_7	0.60	1.20	0.06	−0.10
St	TCS	2.31	0.39	6.93	0.13	1.00	−0.80	0.09	−0.21
AN	TCS	0.30	0.36	0.90	0.12	0.60	1.20	0.11	−0.29

* $r_1'=3r_1$, $r_2'=r_2/3$.

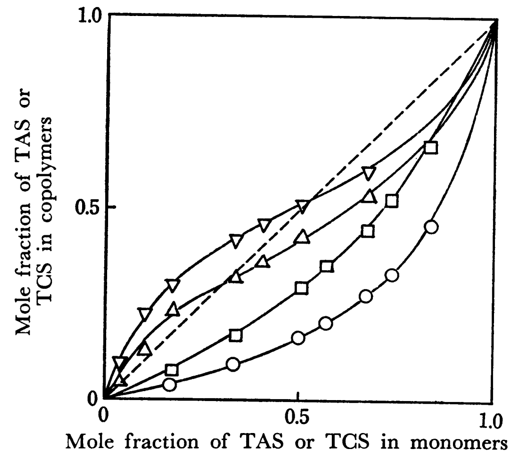

Fig. 7. Monomer-polymer composition curves.
○: St-TAS, △: AN-TAS, □: St-TCS, ▽: AN-TCS,
——: logical curve

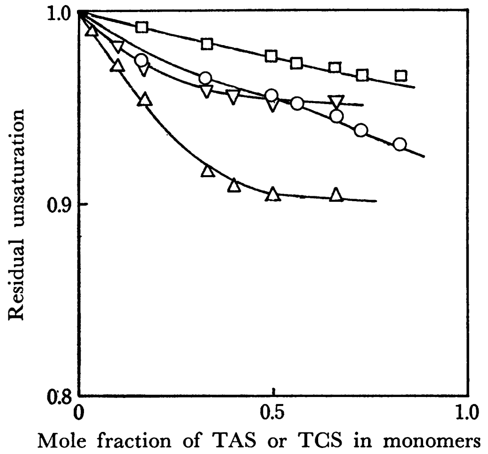

Fig. 8. Plots of residual unsaturation against the monomer composition.
○: St-TAS, △: AN-TAS, □: St-TCS, ▽: AN-TCS

No difference in Q' and e' values between tri- and diallylidene cyclic compounds could be recognized. This suggests that the TAS are unconjugate and neutral monomers just the same as the DAPE.

The Q' values for TCS were slightly larger than those for TAS; they might be influence by the hyperconjugation of the methyl group. On the other hand, the e' values of TCS were more negative than those of TAS; they must be contributed to the methyl group, which is a proton donor.