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### Polymers Containing the s-Triazine Ring. V. Base-Catalyzed Hydrogen-Transfer Polymerization of 2-Vinyl-4,6-diamino-s-triazine [1]

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## **Polymers Containing the s-Triazine Ring. V. Base-Catalyzed Hydrogen-Transfer Polymerization of 2-Vinyl-4,6-diamino-s-triazine [1]**

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### ABSTRACT

2-Vinyl-4,6-diamino-s-triazine (VDAT) was polymerized in aprotic solvents with the basic initiators potassium tert-butoxide (*tert*-BuOK), sodium methoxide, and *n*-butyllithium. It was confirmed by IR and NMR that the polymerization progressed by hydrogen transfer. The catalytic activity decreased in the order cited. In the case of *tert*-BuOK, the mechanism of initiation was investigated by NMR of the polymer obtained at the initial stage and gas chromatographic determination of *tert*-butanol in the reaction mixture, and the mechanism of propagation was investigated by viscosity measurements, copolymerizations with divinyl compounds, and fractionation of the copolymers. The results showed that the initiation started with hydrogen abstraction by the initiator anion, and that propagation proceeded by intermolecular hydrogen transfer.

Since 2-vinyl-4,6-diamino-s-triazine (VDAT) was first prepared by Overberger and Michelotti [2], it has been used for radical homo- and copolymerization [2, 3] and polyaddition [4]. The vinyl group

which is directly attached to the *s*-triazine ring has a lower electron density because of the partial localization of electrons on the ring nitrogens. Therefore, VDAT is expected to be capable of being polymerized by anionic species, but no literature has been found concerning the addition polymerization of VDAT by an anionic mechanism. The basicity of amino groups, on the other hand, is reduced for the same reason, so that the reaction behavior of the amino groups directly linked to the *s*-triazine ring is similar to that of the amide group. The well-known monomers which contain an amide group and polymerize by anionic mechanism through hydrogen transfer are acrylamide [5] and other unsaturated amides [6]. Thus it is possible for VDAT to undergo two types of anionic polymerization: addition polymerization of the vinyl group and hydrogen-transfer polymerization involving both the vinyl and amino group.

In the present study we carried out anionic homo- and copolymerization of VDAT with several anionic initiators and obtained some information concerning the polymer structure and reaction mechanism.

## EXPERIMENTAL

### Materials

VDAT was prepared from  $\beta$ -dimethylaminopropionitrile and dicyandiamide [7]. 2-Methyl-4,6-diamino-*s*-triazine (MDA) was prepared from acetonitrile and dicyandiamide according to the preparation of 2-phenyl derivative [8], mp 267°C. Divinyl sulfone (DVS) was used after distillation on calcium hydride. Guaranteed grades of melamine, *N,N'*-methylene bisacrylamide (BA), and azobisisobutyronitrile (AIBN) were used as received from Wako Pure Chemical Industries, Ltd.

*tert*-BuOK was prepared by dissolving potassium in distilled and dry *tert*-butanol, and by evaporating excess butanol under reduced pressure [9]. The composition of the butoxide was found to be *tert*-BuOK:*tert*-BuOH by volumetric analysis.  $\text{CH}_3\text{ONa}$  was similarly prepared from sodium and dry methanol. *n*-BuLi in ~20% hexane solution was purchased from Merck. Its concentration was determined by volumetric titration before use.

Dimethylsulfoxide (DMS) and hexamethylphosphoramide (HMPA) were dried on calcium hydride and distilled under reduced pressure. They were stored under nitrogen atmosphere and pipetted off in a nitrogen stream.

## Polymerization

Homopolymerization of VDAT. A typical example using *tert*-BuOK as initiator follows.

In a nitrogen-replaced ampule were added 0.309 g (2.25 mmoles) of VDAT, 0.0225 g (0.14 mmole) of the initiator, 0.01 g of hydroquinone (HQ), a radical inhibitor, and 10 ml of DMSO in this order in a nitrogen stream. The ampule was degassed by the usual freeze-thaw technique, sealed, and heated at 100°C for 20 min in a thermostatted oil bath. The seal was broken and a few drops of formic acid was added in order to terminate the reaction. The mixture was poured into a large quantity of diethyl ether (which could be replaced by methanol). The precipitated white solid was filtered, dispersed in methanol with occasional stirring for a few hours, again filtered, and dried. The yield was 0.169 g (54.7%). Other runs were conducted with varying reaction conditions of solvent, temperature, time, and initiator concentration. The polymers were insoluble in common organic solvents but soluble in mineral acids and formic acid.

The same procedure was followed in the case of  $\text{CH}_3\text{ONa}$ . With the *n*-BuLi system a 100-ml three-necked flask was used instead of an ampule.

Copolymerization of VDAT. In a nitrogen-replaced 200 ml three-necked flask were placed 1.122 g (8.18 mmoles) of VDAT, 1.239 g (8.04 mmoles) of BA, 0.01 g of HQ, and 50 ml of DMSO. The mixture was stirred mechanically until the whole solids were dissolved. Then 0.377 g (2.03 mmoles) of *tert*-BuOK and 40 ml of DMSO were added to the mixture, which was further stirred until the initiator was dissolved. The flask was heated at 100°C for 2 hr with stirring under nitrogen. The reaction mixture was then treated in a manner similar to the case of homopolymerization. The yield was 1.609 g (68.2%, No. VTBA-8). The copolymer was soluble in mineral acids, formic and acetic acid, and hot DMSO.

Copolymerization of VDAT with DVS, DVS with MDA, and DVS with melamine was carried out by a similar procedure. VDAT-DVS copolymers were soluble in DMF, formic acid, and mineral acids in addition to DMSO. Other copolymers were soluble in mineral acids and hot DMSO.

Fractionation. The product of the run No. VTBA-8 (Table 6) was submitted to fractional precipitation. On slight heating, 1.5 g of the product dissolved in 40 ml of DMSO. The solution was allowed to cool to room temperature. Methanol (28 ml) was added with magnetic stirring, and the system was heated slightly and stirred at room temperature for 12 hr. The precipitate was collected by filtration. The filtrate was treated successively in a very similar manner with different quantities of methanol: 8, 5, and 20 ml. Four fractions

were obtained. Fractional precipitation was also applied to the VDAT-DVS copolymer (Table 6). It was separated into four fractions.

Preparation of VDAT Homopolymers at Different Reaction Intervals. Solution A was prepared in a 200-ml three-necked flask under nitrogen. It was composed of 1.177 g (8.85 mmoles) of VDAT, 0.03 g of HQ, and 110 ml of DMSO. In another 200 ml three-necked flask were placed 0.132 g (0.71 mmole) of *tert*-BuOK and 65 ml of solution A under nitrogen. The initiator was dissolved with mechanical stirring at room temperature. The reaction solution was then heated at 60°C for 30 min and 25 ml of the solution was pipetted off. This aliquot, after the addition of a few drops of formic acid, was poured into methanol. Solution A (40 ml) was added to the rest of the reaction solution. After 3 min, 25 ml of the solution was pipetted off and poured into methanol. Another 25 ml was taken out at 8 min after the addition of solution A. At 18 min the remainder was poured into methanol. Each of the four fractions was reprecipitated from formic acid-dilute sodium hydroxide solution.

### Measurements

The determination of *tert*-butanol in the polymerization mixtures was carried out by gas chromatography. *sec*-Butanol was added as internal standard to the polymerization mixtures acidified with acetic acid. The mixture was stirred and analyzed using a Hitachi Model K23 gas chromatograph with a 2-m packed column containing 15% dioctyl sebacate and maintained at 100°C. The amount of *tert*-butanol was estimated from the calibration line obtained from a varying ratio of *tert*-butanol to *sec*-butanol under the same chromatographic conditions. The acidified initiator solutions were also analyzed.

NMR spectra were recorded with a Japan Electron Optics Lab. Model JNM-4H-100 high resolution spectrometer at 100 MHz in trifluoroacetic acid solution at room temperature with tetramethylsilane as internal standard.

IR spectra were recorded with a Hitachi Model 215 IR spectrophotometer by the usual KBr method.

## RESULTS AND DISCUSSION

### Hydrogen-Transfer Polymerization

The homopolymerization results of VDAT with three different anionic initiators and a radical initiator, AIBN, are presented in

Table 1. The products had the IR patterns shown in Fig. 1. VDAT shows the distinct absorptions at  $3200$  and  $3350\text{ cm}^{-1}$  due to  $\text{NH}_2$  stretching, at  $1650\text{ cm}^{-1}$  due to  $\text{NH}_2$  deformation, and at  $960$  and  $990\text{ cm}^{-1}$  due to a vinyl group. All of them are greatly reduced in their intensity in PVT-15 and PVTM-6, indicating that both of the vinyl and amino group reacted, whereas PVTA-1 prepared with

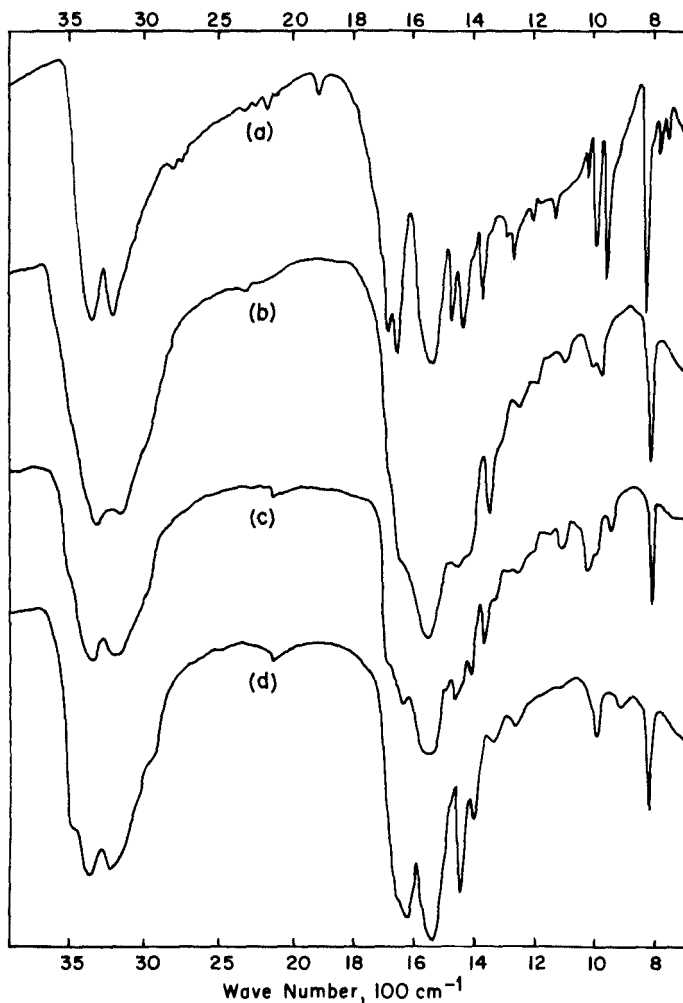


FIG. 1. IR spectra of (a) VDAT, (b) PVT-15, (c) PVTM-6, and (d) PVTA-1.

TABLE 1. Polymerization of VDAT with Anionic Initiators and AIBN

Initiator	Temp. (°C)	No.	$\frac{[\text{Initiator}]}{[\text{VDAT}]}$	VDAT (mole/liter)	Time (min)	Yield (%)	$\eta_{sp}/c^a$
tert-BuOK	60	PVT-26	0.14	0.18	30	95.4	
	60	PVT-25	0.13	0.18	60	99.0	
	100	PVT-15	0.62	0.18	5	95.9	
	100	PVT-6	0.06	0.23	20	54.7	0.034
	100	PVT-8	0.06	0.25	60	85.2	0.040
	100	PVT-9	0.06	0.22	120	86.0	0.039
	100	PVTH-1 <sup>b</sup>	0.13	0.18	5	82.3	0.039
	60	PVTM-6	0.20	0.23	30	62.9	0.026
	60	PVTM-3	0.21	0.20	60	89.0	0.026
CH <sub>3</sub> ONa	60	PVTM-5	0.18	0.25	240	98.0	0.028
	100	PVTM-2	0.69	0.21	30	94.6	0.038
	60	PVTB-8	0.21	0.18	240	11.3	0.011
n-BuLi	60	PVTB-7	0.20	0.18	300	31.9	0.021

100	PVTB-12	0.20	0.18	15	43.0	0.027
100	PVTB-6	0.20	0.18	30	71.4	0.036
100	PVTB-11	0.20	0.18	50	80.1	0.035
AIBN	PVTA-1	0.01	0.17	120	69.5	

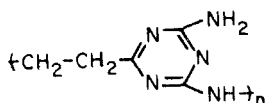
<sup>a</sup> c  $\approx$  0.5 g/dl in 2 N HCl at 25°C except for PVT at 30°C.

<sup>b</sup> In HMPA.



AIBN still has strong  $\text{NH}_2$  absorptions. The products obtained with  $n\text{-BuLi}$  also had a pattern very similar to that of PVT-15 and PVTM-6. No clear difference was observed among the anionically produced samples listed in Table 1, but there was a slight decrease in the intensity of and the broadening of  $\text{NH}_2$  absorptions under severer conditions.

Figure 2 shows the NMR spectra of PVT-15, PVT-8, and PVTA-1. The former two are clearly different from the latter in which peaks are assigned as  $\delta 2.40$ ,  $\text{C}-\text{CH}_2-\text{C}$ ;  $\delta 3.03$ ,  $\text{CH}$ -ring; and  $\delta 7.75$ ,  $\text{NH}_2$ . In the two anionically produced samples the area ratio at  $\delta 3.25$ , 4.15, and 7.75 was nearly 2:2:3, suggesting that the polymer had the structure



I

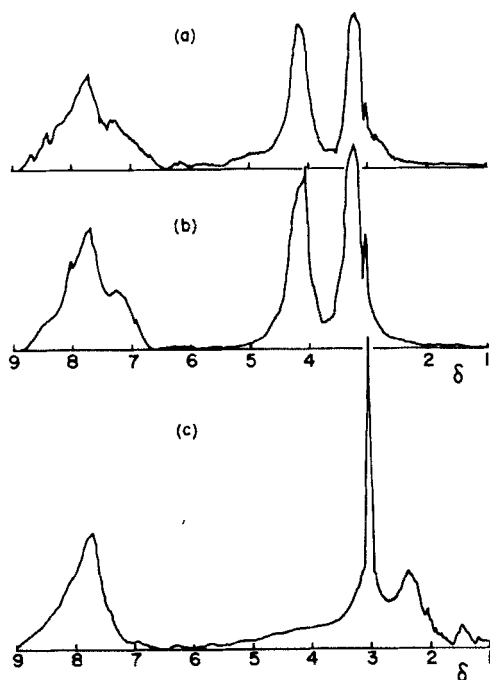
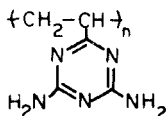


FIG. 2. NMR spectra of (a) PVT-15, (b) PVT-8, and (c) PVTA-1.

Those peaks can be assigned as  $\delta 3.25$ ,  $\text{CH}_2$ -ring;  $\delta 4.15$ ,  $\text{N}-\text{CH}_2-\text{C}$ ; and  $\delta 7.75$ ,  $\text{NH}$  and  $\text{NH}_2$ . All of these facts derived from IR and NMR strongly support Structure I, but not the following one by addition polymerization:



II

The extent of the incorporation of the radically formed Structure II to Structure I was examined in the absence of any initiator as a control reaction. The results are summarized in Table 2. PVTQ-1 gave no precipitate in methanol after the reaction, while PVTQ-2 of very high VDAT concentration had a little precipitate. The VDAT concentration in PVTQ-1 was approximately the same as that in Table 1. The anionically formed Structure II may also be ruled out because the areas in NMR agreed with those of the Structure I, and *tert*-butanol was formed quantitatively as is described later. Consequently, the products obtained with anionic initiators essentially have Structure I.

The catalytic activity of the three anionic initiators, compared in Fig. 3, decreases in the order *tert*-BuOK >  $\text{CH}_3\text{ONa}$  > *n*-BuLi, even when small differences in the ratio of the initiator to monomer and monomer concentration in Table 1 are taken into consideration. This tendency agrees with the results of earlier work [10]. Addition

TABLE 2. Polymerization of VDAT in the Absence of Initiator or in the Presence of Water

No.	$\frac{[\textit{tert}\text{-BuOK}]}{[\text{VDAT}]}$	VDAT (mole/liter)	Temp. (°C)	Time (min)	Yield (%)
PVTQ-1 <sup>a</sup>	0	0.18	100	120	0
PVTQ-2 <sup>a</sup>	0	0.63	100	60	4.7
PVTN-1 <sup>b</sup>	0.29	0.19	60	40	90.3

<sup>a</sup>HQ: 8.7 mole % based on VDAT.

<sup>b</sup>Water, 2.22 mmoles; *tert*-BuOK, 0.56 mmoles; VDAT, 1.92 mmoles.

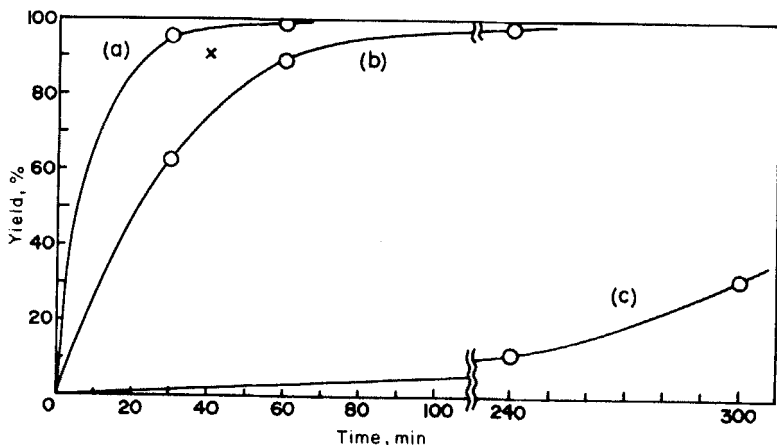


FIG. 3. Yield against time in DMSO at 60°C: (a) *tert*-BuOK, (b) CH<sub>3</sub>ONa, and (c) *n*-BuLi. (x) PVTN-1.

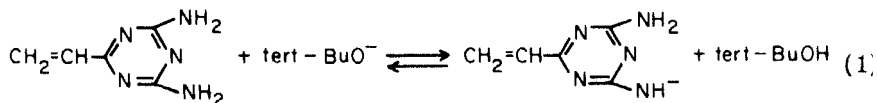
of water to a *tert*-BuOK system also brought about the VAT polymer (PVTN-1 in Table 2) which showed an IR pattern very similar to that of other hydrogen-transfer products. This suggests that potassium hydroxide is also able to initiate the polymerization. Similar results were reported in the polymerization of acrylamide by *sec*-BuONa with the addition of water [11].

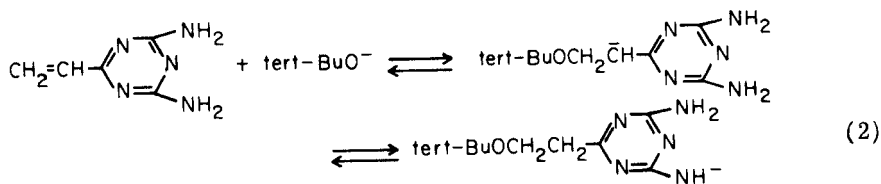
### Mechanism of Hydrogen Transfer

This subject has been extensively studied for acrylamide and its derivatives, and has been in controversy [12] since Breslow first proposed it [5]. In initiation there are two possibilities: abstraction of amine hydrogen by initiator anion and addition of the anion to the carbon-carbon double bond of the amide. Propagation also has two possibilities: stepwise intermolecular transfer and intramolecular transfer, which has the features of chain-growth polymerization. Which of the two actually takes place in both initiation and propagation was examined for *tert*-BuOK in the present study.

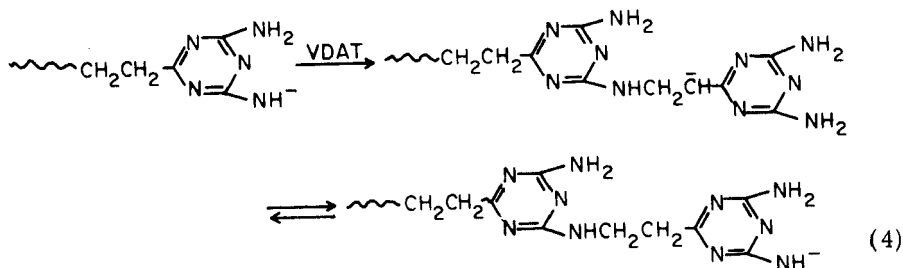
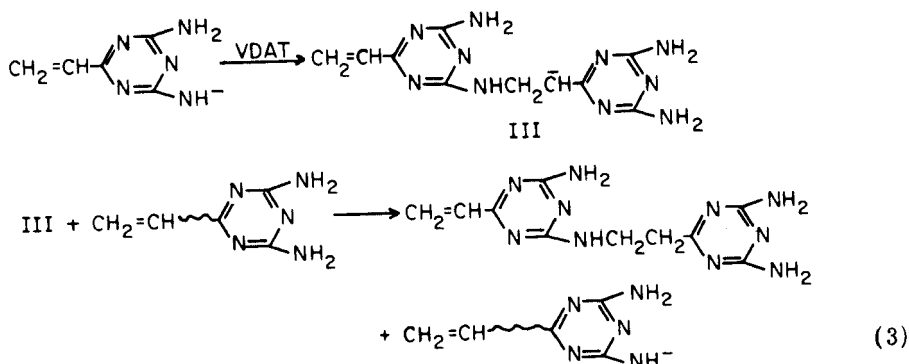
According to the above discussion, VAT can react as follows.

Initiation:





Propagation:



For initiation, the *tert*-butoxy group in the initial product was examined by NMR, and the quantity of *tert*-butanol in the reaction mixture was determined by gas chromatography. As is shown in Table 1, PVT-15 with a large quantity of the initiator gave nearly quantitative conversion in a very short time. The NMR spectrum of PVT-15 (Fig. 2) did not show any signal for the *tert*-butoxy group which was clearly observed at  $\delta 1.33$  for *tert*-butanol in the same solvent. This fact indicates the absence of the *tert*-butoxy group at the polymer ends.

The chromatographic results are tabulated in Table 3. In all runs an amount very close to that calculated from the charged initiator

TABLE 3. Determination of tert-Butanol by Gas Chromatography<sup>a</sup>

No.	tert-BuOK (mole/liter)	VDAT (mole/liter)	$\frac{[\text{tert-BuOK}]}{[\text{VDAT}]}$	Shaking at room temp. (min)	Shaking, min (°C)	$\frac{[\text{tert-BuOK}] \text{ found}}{2([\text{tert-BuOK}] \text{ charged})}$
PVTC-3	0.12	0.20	0.60	30	5(90-100)	0.927
PVTC-4	0.18	0.30	0.60	30	5(90-100)	1.038
PVTC-5	0.30	0.50	0.60	60	-	1.055
PVTC-2	0.45	0.18	0.25	10	10(60)	1.023
B-1	0.29	0				1.004
B-2	0.29	0				1.015

<sup>a</sup>The solutions were acidified with AcOH after shaking.

was found. The reliability was checked in runs B-1 and B-2 with the initiator alone. This is in accord with the results of volumetric analysis. All these results support initiation with hydrogen abstraction by the initiator anion [Eq. (1)].

The mechanism in propagation was investigated by viscosity change and copolymerizations. If the chain grows through hydrogen abstraction (chain transfer), the addition of the monomer in the course of polymerization will greatly reduce the average chain length. Intramolecular hydrogen transfer and addition polymerization, on the other hand, will not decrease but will increase the chain length. As is summarized in Table 4, the addition of VDAT after 60 min gave an increase in viscosity in 3 min, a considerable decrease in 8 min, and a gradual increase thereafter. The increase at 3 min can be attributed to the addition of new VDAT to  $\bar{N}H$  at the polymer end, which is probably present in a larger quantity due to the smaller reactivity of  $\bar{N}H$  than of carbanion. The sudden and considerable decrease at 8 min indicates the occurrence of chain transfer and may support intermolecular hydrogen transfer [Eq. (3)]. This observation and the quantitative formation of tert-butanol (Table 3) can also rule out the incorporation of the anionically formed Structure II. Since viscosity, however, is influenced by not only the average chain length but also by a very small number of conspicuously large sized molecules, further evidence for the intermolecular hydrogen transfer was obtained from copolymerizations. VDAT reacted with BA and DVS to give products with the composition and in the yield listed in Table 5. In order to examine whether the products are copolymers or not,

TABLE 4. Reduced Viscosity of VDAT Polymers Obtained at Different Intervals after the Addition of VDAT in the Course of Polymerization<sup>a</sup>

No.	Time (min)	Yield (%)	$\eta_{sp}/c^b$
PVT-38a	60	87.5	0.134
PVT-38b	3 <sup>c</sup>	45.6	0.144
PVT-38c	8 <sup>c</sup>	58.2	0.121
PVT-38d	18 <sup>c</sup>	-	0.130

<sup>a</sup>Reaction conditions: [tert-BuOK]/[VDAT] = 0.14; VDAT, 0.08 mole/liter, 60°C.

<sup>b</sup>In 85% formic acid at 25°C,  $c \approx 0.5$  g/dl.

<sup>c</sup>After the addition of solution A.

TABLE 5. Copolymerization of VDAT with BA and DVS<sup>a</sup>

No.	VDAT charged (mole fraction)	Yield (%)	VDAT in the copolymer <sup>b</sup> (mole fraction)
VTBA-10 <sup>c</sup>	0.19	57.5	0.29
VTBA-11	0.35	65.4	0.41
VTBA-12	0.65	78.7	0.56
VTBA-9	0.80	97.9	0.69
VTVS-6 <sup>d</sup>	0.65	96.2	0.68
VTVS-2	0.49	85.7	0.61
VTVS-7	0.34	104	0.35
VTVS-5	0.18	87.0	0.22

<sup>a</sup>Total monomer concentration, 0.18 mole/liter; tert-BuOK, 0.12 to 0.13 mole % based on monomers.

<sup>b</sup>Obtained from elemental analysis.

<sup>c</sup>With BA at 100°C for 15 min. Homopolymerization of BA under the above conditions for 2.5 hr gave 61% yield.

<sup>d</sup>With DVS at 60°C for 30 min. Homopolymerization of DVS with 0.2 mole % tert-BuOK at 100°C for 2 hr gave no precipitate in methanol.

fractional precipitation and analyses of the fractions were carried out. The results are summarized in Table 6. The composition of the fractions did not vary substantially, and the IR patterns did not show a clear difference before and after fractionation and among those fractions. Typical patterns are shown in Fig. 4 (a and b), where the peaks characteristic to comonomers appear, such as 1630-1650  $\text{cm}^{-1}$  for amide and 2940  $\text{cm}^{-1}$  for methylene in Fig. 4(a) and 1120 and 1300  $\text{cm}^{-1}$  for sulfone, 2950-3000  $\text{cm}^{-1}$  (weak) for methylene in Fig. 4(b), and  $\sim 1560 \text{ cm}^{-1}$  for s-triazine ring in both spectra. The products were soluble in DMSO and other solvents in which poly(VDAT) was not soluble. All these results indicate that the products in Table 5 are copolymers formed by intermolecular hydrogen transfer. The composition of BA or DVS larger than 50% in Table 5 suggests that both of the  $\text{NH}_2$  hydrogens of some VDAT reacted with the comonomers.

TABLE 6. Fractionation of VDAT-BA and VDAT-DVS Copolymers and Analyses of the Fractions

Fraction no.	Weight %	VDAT <sup>a</sup> (mole fraction)
VTBA-8-A <sup>b</sup>	27.4	45.4
VTBA-8-B	5.9	45.0
VTBA-8-C	25.5	47.1
VTBA-8-D	41.2	40.7
VTVS-1-A <sup>b</sup>	14.6	49.9
VTVS-1-B <sup>c</sup>	32.3	41.8
VTVS-1-C <sup>c</sup>	29.7	43.1
VTVS-1-D <sup>d</sup>	23.4	-

<sup>a</sup>Obtained from elemental analysis (N for VTBA and S for VTVS).

<sup>b</sup>Prepared from 1:1 molar mixture at 100°C for 2 hr (yield 68.5% for VTBA-8 and 87.0% for VTVS-1).

<sup>c</sup>Molecular weight by cryoscopic method in DMSO ( $\eta_{sp}/c$  in 85% formic acid at 25°C): 1850 (0.061) for VTVS-1-B and 1310 (0.057) for VTVS-1-C, which correspond to (VDAT)<sub>6.1</sub>(DVS)<sub>8.5</sub> and (VDAT)<sub>4.5</sub>(DVS)<sub>5.9</sub>, respectively.

<sup>d</sup>Precipitated in a large quantity of methanol.

If the intermolecular hydrogen transfer is valid in the propagation, then *s*-triazine comonomer need not have any reactive unsaturated substituent. Thus an attempt was made to use MDA and melamine as comonomers in the copolymerization with DVS. The copolymers were also produced as shown in Table 7, although the yield in MDA was less than in VDAT. The copolymers possessed IR peaks characteristic of the *s*-triazine ring and DVS (Fig. 4c). These additional results, as well as the copolymerizations of VDAT, strongly support the intermolecular hydrogen transfer in the propagation. This conclusion is consistent with the mechanism proposed on the basis of spectroscopic observations for the polymerization of *p*-vinylbenzamide with potassium *tert*-butoxide [13] and *p*-methyl- $\alpha$ -methylstyrene with *n*-BuLi or Na-K alloy [14]. These results seems to be reasonable since a long-range



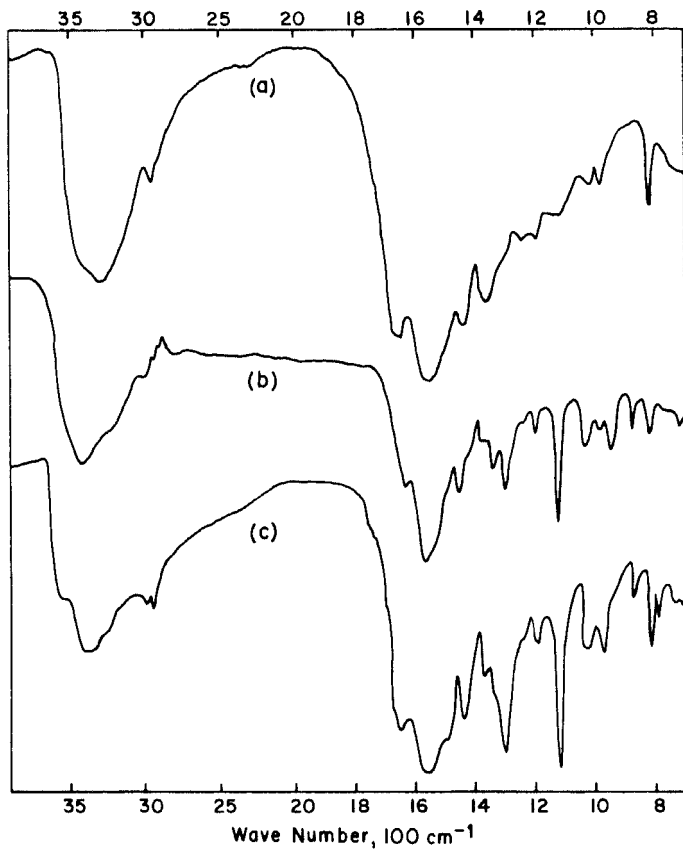


FIG. 4. IR spectra of (a) VTBA-8-A, (b) VTVS-1-A, and (c) VSMD-2.

TABLE 7. Copolymerization of DVS with MDA and Melamine<sup>a</sup>

No.	DVS (mole fraction)	tert-BuOK (mole%)	Yield (%)
VSMD-2	0.499	0.12	13.3
VSMM-1	0.600	0.12	58.4
VSMM-2	0.598	0.07	91.9

<sup>a</sup>At 100°C for 2 hr.

intramolecular hydrogen transfer would be unfavorable for the compounds in which vinyl group and active hydrogens are rather distantly separated.

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