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The Synthesis and Polymerization of 2-(*p*-Vinylphenyl)-4,6-diamino-*s*-triazine[1]

Eizo Oikawa and Kazuya Horiguchi
Faculty of Engineering, Niigata University, Nagaoka, Niigata 940

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Synopsis. A new olefinic *s*-triazine, that cited in the title, was prepared by the reaction of *p*-cyanostyrene with dicyandiamide. Methyl *p*-vinylbenzoate could provide the triazine in an improved yield. The triazine readily underwent radical polymerization in an aprotic solvent to give a soluble and thermally stable polymer.

The reaction of nitriles with dicyandiamide (DCDA) has long been utilized for the preparation of many guanamines. This method has not, however, been successful in the preparation of olefinic guanamines, which contain an unsaturated group attached directly to the ring. However, the use of this method seems possible if one uses an unsaturated nitrile containing another group or atoms between the unsaturated and cyano group, but very few attempts to do so have thus far been reported.[2] We used *p*-cyanostyrene (*p*-CNSt) as such a nitrile in an attempt to prepare polymerizable *s*-triazine compounds; we could thus prepare the new title compound (VPAT), as is summarized in Table 1. In the actual performance of the reaction, a lower reaction temperature is desirable in order to minimize the polymerization of *p*-CNSt, but the precipitation of the white product did not take place for 2 hr, not until the temperature attained 115 °C. Although the reaction was continued for 2 hr, 1 hr appears to be enough from a comparison of SGH–1 with SGH–4. The amount of potassium hydroxide had an influence on the yield. The optimum molar ratio of the catalyst to *p*-CNSt was about 0.25. A higher amount might give rise to unidentified side reactions to a greater degree.

While *p*-CNSt brought a yield of 20% at best, methyl *p*-vinylbenzoate (MVB) increased the yield of VPAT more than double. A basic catalyst, sodium methoxide, did not markedly affect the reaction.

VPAT readily underwent radical polymerization in a good conversion, as will be described in the Experimental section. Comparable intrinsic viscosities were obtained for heterogeneous polymerization in DMF, but a higher viscosity was obtained for a homogeneous polymerization in DMSO.

Poly(VPAT) has a *s*-triazine ring as a side group in every repeating unit. It is possible to introduce the same side group to a polymer possessing cyano groups, but the complete reaction is generally difficult.[3] In our work, at best about 93% of the cyano group of poly(*p*-CNSt) reacted in DMSO at 100°C for 3 hr. In this respect, poly(VPAT) can be regarded as 100% converted poly(*p*-CNSt).

These polymers were soluble only in DMSO and concentrated sulfuric acid, and were insoluble in other common organic solvents. They showed a relatively good thermal stability in air; the weight losses for PVBG–2 were 10% at 350 °C and 15% at 396 °C; for PVBG–4, they were 10% at 375 °C and 15% at 400 °C.

Experimental

*2-(*p*-Vinylphenyl)-4,6-diamino-*s*-triazine (VPAT) from *p*-CNST.* *p*-CNSt was prepared from bromobenzene.[4] The reaction was conducted in a 100-ml, three-necked flask fitted with a mechanical stirrer, a condenser, and a thermometer under the conditions listed in Table 1. Thirty or forty min after the reaction started, white solids were precipitated. After the required period, the reaction mixture was cooled to room temperature. The precipitate was filtered and washed with warm water, methanol, and then nitromethane to remove any unreacted materials and the polymer. When the filtrate was poured into water, a white precipitate was obtained. It was treated similarly. Both solids could be purified by either recrystallization from nitromethane or sublimation under reduced pressure, and were found to be the same product from their melting points and the IR spectra; mp 222—223 °C (in a sealed capillary). Found: C, 61.35; H, 5.25; N, 33.75%; Calcd for $C_{11}H_{11}N_5$: C, 61.96; H, 5.20; N, 32.84%. IR (KBr): NH_2 (3520 w, 3320 m, 3130 s, 1680s, 1640s), *s*-triazine ring (1530—50s, 820m), vinyl (900m, 980w, 995w), NMR (DMSO-d_6): *p*-substituted benzene ring (7.91 δ, q, $J=8$, 4H), NH_2 (6.77 δ, s, 4H), vinyl (6.95—5.30 δ, m, 3H).

Table 1. Reaction of *p*-CNSt with DCDA[a]

No.	SGH-2	SGH-4[b]	SGH-1	SGH-3
p-CNSt mmol	31.0	31.1	38.8	31.2
DCDA mmol	48.0	48.6	65.0	43.0
KOH mmol (mol/l)	3.7 (0.46)	7.3 (0.91)	10.4 (1.04)	14.8 (1.85)
$\frac{[\text{KOH}]}{[p\text{-CNSt}]}$	0.119	0.233	0.268	0.475
Yield %	10.0	19.6	16.0	15.2

a) *p*-*t*-Butylcatechol: 0.1 g (0.6 mmol); Methyl cellosolve: 8—10 ml, 115 °C, 2 hr. b) 115 °C, 1 hr.

VPAT from MVB. MVB was prepared from *β*-bromoethylbenzoic acid.[4–6] The reaction was carried out according to the procedure of Ref. 7. The yield in the case of no catalyst was 41.7% (No. SG–1); mp 225—6 °C (in a sealed capillary). Found: C, 62.04; H, 4.95; N, 32.47%. The addition of sodium to methanol or sodium methoxide (16 mol% based on MVB) afforded the same product in a better yield (48.0%, No. SG–2).

Polymerization of VPAT. The polymerization was carried out in a sealed tube with azobisisobutyronitrile (1.05 mol% based on VPAT) at 80 °C for 5 hr. The DMF solution became turbid in a few minutes, and the polymer started to precipitate. The polymer was purified by reprecipitation from DMSO–methanol. One gram of SGH–2 in 5 ml of DMF gave a yield of 73.3% and an intrinsic viscosity of 0.263 at 25 °C in DMSO (No. PVBG-2), and 0.694 g of

SG-2 in 3.5 ml of DMF gave 91.0% and 0.271 (No. PVBG-3). In 1.8 ml of DMSO, 0.365 g of SGH-4 gave 82.5% and 0.325 (No. PVBC-4).

The weight loss was measured with a solenoid-type thermobalance, Model SE-52, of Tokyo Koki Seizosho.

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