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Cationic Polymerization of N-Vinylcarbazole in the Presence of (+)-D-Camphor-10-sulfonic Acid

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ABSTRACT

Optical rotation values of the polymers of N-vinylcarbazole (VCZ) obtained by a (+)-D-camphor-10-sulfonic acid (DCS) catalyst were found to increase linearly with an increase in the donor numbers of such solvents as 1,2-dichloroethane, dioxane, and tetrahydrofuran and such additives as N,N-dimethylformamide and tetramethylurea. Asymmetric induction is considered to be caused by a stereoselective fixation of the growing VCZ cation with the optically active DCS anion, and fixation is assisted by nucleophilic solvation. No optically active VCZ polymer was obtained by using

p-toluenesulfonic acid as the catalyst and (2S)-N,N'-carbonyl-N-cyclohexyl-aminomethyl pyrrolizine as the additive.

INTRODUCTION

Our preceding papers showed that optically active copolymers are obtained by the free radical copolymerization of maleic anhydride with styrene and isobutyl vinyl ether in 1-menthol [1-3], and N-substituted maleimides in 1-menthol or L-proline derivatives [4]. Recently, Okamoto et al. [5, 6] reported that a highly optically active polymer ($[\alpha]_D^{25} > +250^\circ\text{C}$) is obtained by the anionic polymerization of triphenylmethyl methacrylate in the presence of a (-)-sparteine-butyl-lithium complex. Cationic polymerization was also found to cause asymmetric induction, i.e., in the polymerization of racemic cis-sec-butyl-1-propenylether with (-)-p-menth-3-yloxyaluminum dichloride [7]. This article deals with the reinvestigated results of the cationic polymerization of N-vinylcarbazole (VCZ) in the presence of (+)-D-camphor-10-sulfonic acid (DCS), together with those of our previous work [8].

EXPERIMENTAL

N-Vinylcarbazole (VCZ) was purified by recrystallization from hexane.

(+)-D-Camphor-10-sulfonic acid (DCS), $[\alpha]_D^{25} = +20.6^\circ\text{C}$ ($c = 1.0$, H_2O), was purified by recrystallization from ethyl acetate.

(2S)-N,N'-Carbonyl-N-cyclohexyl-aminomethyl pyrrolizine (I) was prepared by Mukaiyama's method [9], mp $38-40^\circ\text{C}$, $[\alpha]_D^{25} = -62.9^\circ$ ($c = 1.02$, MeOH), m/e 208, IR 1690 cm^{-1} , $^{13}\text{C-NMR}$ (CDCl_3) $\delta = 24.93, 25.51, 30.19, 30.48, 30.60, 42.98, 45.84, 51.15, 56.70, 163.22$.

The polymerization of VCZ was carried out in degassed ampules. The prescribed amounts of monomer, solvent, additive, and catalyst were placed under dry nitrogen in a glass tube which was then sealed in vacuo and placed in a thermostated incubator. After a certain interval, methanol-containing aqueous ammonia was added to precipitate the polymer. This VCZ polymer was dissolved in tetrahydrofuran (THF) and reprecipitated in a large amount of methanol-containing aqueous ammonia. After being washed with water and methanol, the polymer was dried in vacuo at room temperature. This procedure was repeated three times.

The polymer samples were characterized by IR and NMR spectral analyses and elemental analysis.

Optical rotation measurements of the polymer samples were taken with a JASCO model J-20 automatic recording spectropolarimeter equipped with a xenon source.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the cationic polymerization of CVZ at 30°C. Optically active polymers were always obtained when the DCS catalyst was used. These polymers were not contaminated with a DCS unit according to ^1H - and ^{13}C -NMR and IR spectral analyses and elemental analysis, which agreed with the results of our previous study [8].

The solvent effect in the polymerization is very interesting. The yield of the polymer increased with an increase of the dielectric constant (ϵ) of the solvent used, i.e., in the order of dioxane (DIX) ($\epsilon = 2.21$), THF ($\epsilon = 7.39$), and 1,2-dichloroethane (DCE) ($\epsilon = 10.37$), but the α values of the polymers were not related to the solvent polarity. It is interesting to note, however, that the values seem to increase with increasing donor number (DN) of the solvent, i.e., in the order of THF (DN = 20.0), DIX (DN = 14.8), and DCE (DN = 0). This means that a nucleophilic solvation of the VCZ cation may play an important role in the asymmetric induction. If this argument is valid, the degree of the asymmetric induction is expected to be increased by a solvent with a higher DN value. However, no polymer was obtained in *N,N*-dimethylformamide (DMF, DN = 26.0), perhaps due to the higher basicity of DMF. Therefore, the effects of such additives as DMF and tetramethylurea (TMU, DN = 31.2) instead of the solvent were investigated. The α values of the polymers were clearly enhanced by the additives (Runs 7 and 8 compared with Run 3) and a linear relationship was obtained between the α values of the polymers and the DN values of the solvents and additives as shown in Fig. 1, indicating the importance of nucleophilic solvation to the DCS cation. Thus, asymmetric induction may also be achieved with an optically active nucleophilic additive. However, an optically inactive polymer was obtained when the optically active amide I was added to the PTS system (Run 9) and the α value of the polymer obtained by adding I to the DCS system (Run 10) was nearly equal to that of the TMU-DCS system (Run 8). It is noted that the optically active polymer has no helical conformation but an asymmetric center in the polymer chain because the α values of the polymers varied only slightly with the solvent and temperature [8].

These results indicate that asymmetric induction is caused by stereoselective fixation of the growing VCZ cation by the optically active DCS anion and that this fixation is assisted by nucleophilic solvation.

TABLE 1. Cationic Polymerization of N-Vinylcarbazole at 30°C^a

Run	Catalyst (mmol)	Amide (mmol)	Solvent	Yield (%)	η_{sp}/c (dL/g) ^b	$[\alpha]_D^{26C}$
1	PTS (0.52)	-	THF	57.4	-	0
2	DCS (0.06)	-	THF	30.3	0.08	+1.92°
3	DCS (0.52)	-	THF	43.8	0.05	+5.44°
4	DCS (2.58)	-	THF	10.8	0.06	+3.36°
5	DCS (0.52)	-	DIX	9.1	0.07	+3.29°
6	DCS (0.52)	-	DCE	82.6	0.15	+0.24°
7	DCS (0.52)	DMF (0.52)	THF	31.4	-	+6.89°
8	DCS (0.52)	TMU (0.52)	THF	35.7	-	+7.64°
9	PTS (0.52)	I (0.52)	THF	54.4	-	0
10	DCS (0.52)	I (0.52)	THF	35.0	-	+7.41°

^aAmount of monomer, 5.2 mmol; total volume, 20 mL; polymerization time, 24 h.

^bSolvent: tetrahydrofuran (THF), 30°C, c = 0.05/100 mL.

^cC = 0.8-1.2 cg/mL; THF.

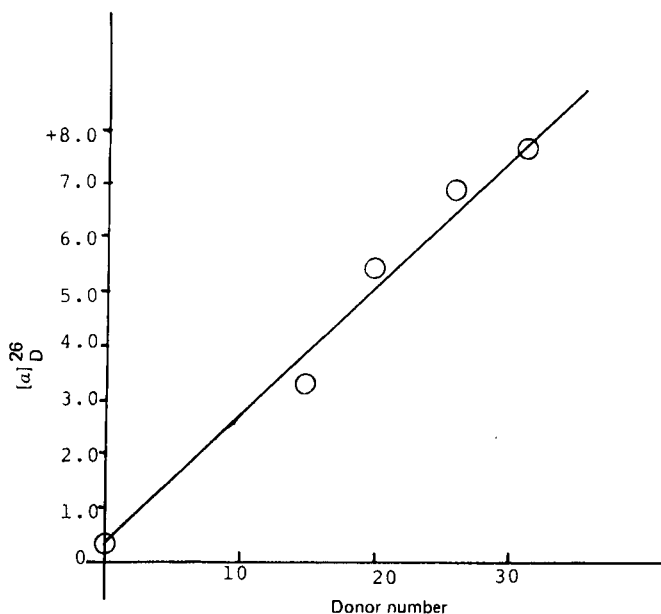


FIG. 1. Relationship between the α values of the polymers and the donor number values of the solvents and additives.

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