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PREPARATION OF POLYMERS WITH SULFILIMINE STRUCTURE

Hideo KISE, Hajime SERITA1), Manabu SENŌ, and Teruzo ASAHARA
Institute of Industrial Science, The University of Tokyo
Minato-ku, Tokyo 106

The reaction of poly(p-vinylbenzylalkyl sulfide) and poly(p-vinylbenzylphenyl sulfide) with chloramine-T afforded polymers with pendant groups of sulfilimine structure. The same polymers were obtained by radical polymerization of N-tosyl-S-alkyl- and N-tosyl-S-phenyl-S-p-vinylbenzylsulfilimines.

The development of synthetic polymers with a variety of functional groups is a matter of current interest in polymer chemistry. There have been many studies on the polymers with sulfonium groups, but little has been reported on the polymers with ylide structures. Tanimoto et al2) carried out the reaction of a sulfonium polymer, poly(p-vinylphenyldimethylsulfonium methyl sulfate), with benzaldehyde in the presence of base and obtained styrene oxide in 76 % yield. The reaction was considered to proceed via the ylide polymer, poly(p-vinylphenylmethylsulfonium methylide), which may be unstable and has not been isolated. This letter describes the synthesis of a new kind of ylide polymers which have stable sulfilimine (sulfur-nitrogen ylide)structure as pendant groups.

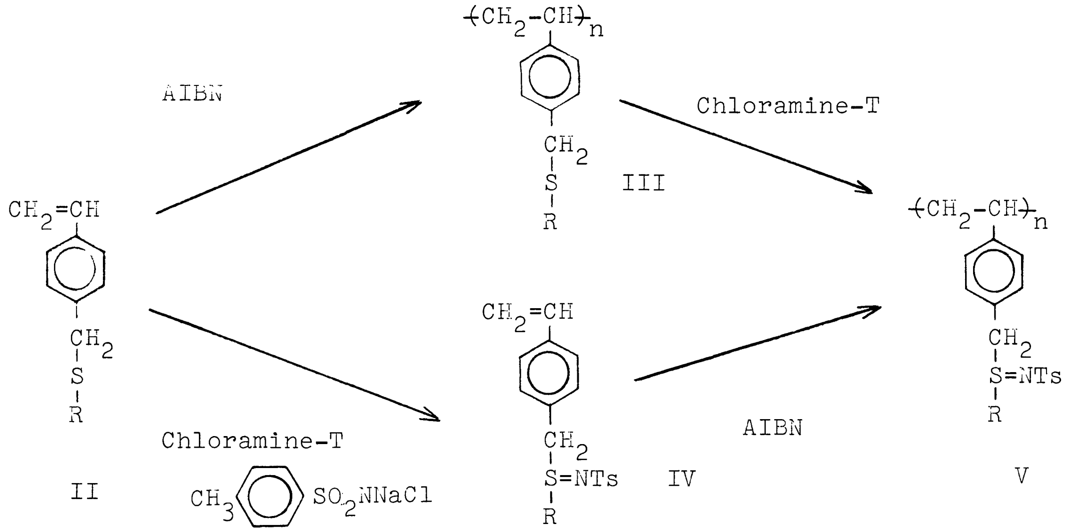
The structure of sulfilimines has been extensively investigated3-8) by X-ray, IR, UV, NMR, and ESCA, and it has been concluded that the S-N bonding in sulfilimines has a semipolar character which is best represented by a resonance structure between Ia and Ib.

$$R_1R_2S{=}NR_3 \longleftrightarrow R_1R_2\overset{+}{S}{-}\overset{-}{N}R_3$$

Ia Ib

The chemical lability of the sulfilimine depends largely on the nature of the substituent R_3; the delocalization of the negative charge on nitrogen atom by R_3 increases the stability and decreases the nucleophilicity of the ylide. In our present work, tosyl group on nitrogen atom was employed to introduce the sulfilimine structure to vinyl polymers because of the facility of the synthetic reaction and the stability of the resulting ylide polymers. Chart 1 outlines the sequence of the reactions.

Chart 1



Ts=p-Toluenesulfonyl; R=Me, Et, Ph

The polymerization of the sulfide II9) with 2,2'-azobisisobutyronitrile (AIBN) gave the polymer III, soluble in CCl_4 and insoluble in n-hexane, which was then treated with chloramine-T in CCl_4-MeOH at refluxing temperature for 5 hrs. The reaction mixture was then poured into a cold 1 % NaOH solution, and the polymer Va was separated, washed with water and dried. An alternative pathway to the polymer V is the reaction of the sulfide II with chloramine-T to give the ylide monomer IV, which was followed by polymerization with AIBN in DMSO to afford the polymer Vb. The polymers Va and Vb are soluble in DMF, DMSO, and $CHCl_3$. The intrinsic viscosity, softening temperature, and microanalysis of III, Va, and Vb are summerized in Table 1. The IR spectra of Va and Vb show the characteristic absorption band of S-N stretching vibration at 946-974 cm^{-1} along with the band of SO_2 group at 1134-1140 (sym), 1086 (asym), and 1274-1280 cm^{-1} (asym). The UV spectra have λ_{max} at 220-227 nm with $\varepsilon = (3.17 \sim 3.35) \times 10^4$.

The microanalyses of the polymers Va agree well with the sulfilimine structure indicating that the sulfide groups in the polymers III were almost completely converted to the sulfilimine groups. The Table indicates also that the monomers IV were successfully polymerized without loss of sulfilimine structure, although the smaller values of the viscosity of Vb suggest the lower degree of polymerization than Va.

N-Tosylsulfilimines are known to be much more stable and less nucleophilic than S-C ylides, but some degree of interaction of sulfilimines with electrophilic reagent is expected, and the interaction of the ylide polymers V with metal ions is under investigation.

As for the chemical modification of polyalkylene sulfides, Price and Blair10) reported the oxidation of polythiethane by hydrogene peroxide to the corresponding

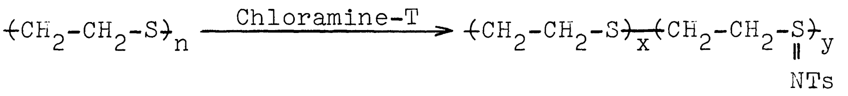
Table 1. Properties and Microanalyses of III, Va, and Vb.

	R	Inherent viscosity*	Softening point(°C)	Found(%) C	Found(%) H	Found(%) N	Calcd.(%) C	Calcd.(%) H	Calcd.(%) N
III	Me	0.248	87-110	73.18	7.22	-	73.12	7.36	-
	Et	0.230	74-109	73.75	7.70	-	74.10	7.96	-
	Ph	0.130	49-62	79.63	6.12	-	79.60	6.23	-
Va	Me	0.174	129-154	60.82	5.45	3.94	61.23	5.74	4.20
	Et	0.169	115-128	61.94	5.68	3.81	62.22	6.09	4.03
	Ph	0.125	51-66	66.53	5.28	3.29	66.81	5.35	3.54
Vb	Me	0.0337	131-151	60.90	5.93	3.98	61.23	5.74	4.20
	Et	0.0911	90-102	62.30	6.13	4.10	62.22	6.09	4.03
	Ph	0.107	46-64	66.81	5.63	3.21	66.81	5.35	3.54

* Measured in DMSO at 30°C for Va and Vb, and in CCl_4 at 30°C for III.

sulfoxide and sulfone polymers. Similar reaction of several polyalkylene sulfides was also carried out by Stille and Empen(11), and sulfone polymers were obtained in fairly good yields.

We attempted the reaction of polyethylene sulfide (PES) with chloramine-T in order to obtain the polymers with sulfilimine structure along the polymer chain shown as follows:



$$\left(CH_2-CH_2-S\right)_n \xrightarrow{\text{Chloramine-T}} \left(CH_2-CH_2-S\right)_x\left(CH_2-CH_2-\underset{\underset{NTs}{\|}}{S}\right)_y$$

In contrast to the polymer III, when PES was treated with chloramine-T, only 1-5 % of the sulfide linkages in PES were converted to the sulfilimine structure.(12) The reaction is inhomogeneous and the small conversion may be due to the low solubility of PES in organic solvents. The reaction of other polyalkylene sulfides is currently under investigation.

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12) The reaction was carried out with slight excess of chloramine-T at 10 - 110°C in MeOH, $MeOH-H_2O$, EtOH, AcOH, HCOOH, and DMF. The conversion of the sulfide linkages to sulfilimine structure was estimated by microanalysis. The best conversion of 5 % was obtained using $MeOH-H_2O$ as a solvent at room temperature.

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