NOTE

Synthesis of Poly(amide-sulfide)s by Polyaddition of Dithiols to *N,N'*-Methylenebisacrylamide

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The facile additions of nucleophiles to compounds containing vinyl double bonds activated by electron-withdrawing groups are well documented in the literature. Using bifunctional compounds, these reactions were utilized for the synthesis of various linear polymers. For example, Michael-type polyaddition of aromatic primary diamines, as well as aliphatic primary monoamines and secondary diamines, to bisacrylamides yielded poly(amide-amine)s of high molecular weight.^{1–3} The base-catalyzed polyaddition of dithiols to bisacrylamides leading to poly(amide-sulfide)s has also been reported;^{2,4,5} however, only low molecular weight polymers were obtained from *N,N'*-methylenebisacrylamide. This article describes the successful synthesis of poly(amide-sulfide)s of high molecular weights by the polyaddition of dithiols to *N,N'*-methylenebisacrylamide.

EXPERIMENTAL

Materials

N,N'-Methylenebisacrylamide (MBAA) was obtained commercially and purified by two recrystalli-

zations from acetone; white needles, mp 183°C with polymerization [lit.⁶ mp 185°C]. IR (KBr) 3290 cm⁻¹ (N–H), 1660 cm⁻¹ (C=O), and 1620 cm⁻¹ (C=C).

1,6-Hexanedithiol (HDT), *p*-xylene- α,α' -dithiol (PXDT), and 4,4'-oxybisbenzenethiol (OBBT) were prepared according to a procedure reported previously.⁷ 1,10-Decanedithiol (DDT), which is commercially available, was purified by distillation before use.

All solvents including *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), and dimethyl sulfoxide (DMSO) were purified in the usual way.

Polymerization

A typical procedure is given as follows for the polymerization with HDT. A mixture of 0.385 g (2.5 mmol) of MBAA, 0.376 g (2.5 mmol) of HDT, 0.15 g (2.5 mmol) of KF, and 0.22 g (5 mmol) of LiCl in 5 ml of HMPA was stirred at room temperature under nitrogen. During the polymerization, the viscosity of the mixture gradually increased. Stirring was continued for 24 h and the mixture was transferred to a large volume of water to precipitate the polymer. The precipitate was collected, washed successively with water and hot acetone, and dried. The yield was 0.70 g (92%). Inherent viscosity of the polymer in *m*-cresol was 0.41 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C. IR (KBr) 3280 cm⁻¹ (N–H) and 1635 cm⁻¹ (C=O).

Anal. Calcd for (C₁₃H₂₄N₂O₂S₂)_n: C, 51.28%; H,

Table I. Polyaddition of dithiols to MBAA

Dithiol	Reaction conditions ^a				Polymer	
	Solvent	Catalyst ^b	Temp	Time	Yield	η_{inh}^c
			°C	h	%	dl g ⁻¹
HDT	DMF	KF + LiCl	20	24	90	0.21
HDT	HMPA	KF + LiCl	20	24	92	0.41
HDT	HMPA	KF + LiCl	60	1	92	1.45
DDT	HMPA	KF	60	1	84 ^d	0.20
DDT	HMPA	LiCl	60	3	92	0.31
DDT	HMPA	LiF	60	3	91	0.16
DDT	HMPA	KF + LiCl	60	1	95	0.60
DDT	HMPA	KF + LiCl	60	3	95	0.76
DDT	HMPA	Et ₃ N + LiCl	50	3	98	0.70 ^e
DDT	DMAc	KF + LiCl	50	3	96	0.52 ^e
DDT	NMP	KF + LiCl	50	3	92	0.50 ^e
DDT	DMSO	KF + LiCl	50	3	97	0.51 ^e
PXDT	HMPA	KF + LiCl	60	24	94	0.16
PXDT	NMP	Et ₃ N + LiCl	50	24	99	0.12
PXDT	NMP	Pip + LiCl	20	24	98	0.21
OBBT	NMP	KF + LiCl	20	24	96	0.10
OBBT	HMPA	Et ₃ N + LiCl	70	24	99	0.14
OBBT	HMPA	Pip + LiCl	70	24	99	0.12

^a Polymerization was carried out with 2.5 mmol of each monomer in 5 ml of the solvent in the presence of the catalyst under nitrogen.

^b Amount of the catalyst: KF, 2.5 mmol; LiCl and LiF, 5 mmol; Et₃N (triethylamine) and Pip (piperidine), 0.5 mmol.

^c Measured at a concentration of 0.5 g dl⁻¹ in *m*-cresol at 30°C.

^d Precipitation occurred during the polymerization.

^e Partial gelation.

7.95%; N, 9.20%. Found: C, 50.9%; H, 7.6%; N, 8.6%.

RESULTS AND DISCUSSION

It was reported that fluoride ion has a marked effect on Michael addition owing to its high capacity to form hydrogen bonds.⁸ This has been successfully applied to the KF-catalyzed polyaddition of dithiols to divinyl sulfone giving high molecular weight polymers.⁷

The polymerization of MBAA with DDT was first carried out in HMPA, using of KF as a catalyst (Table I). In this case, the polymer precipitated from the reaction mixture at an early stage of the polymerization, thus limiting the molecular weight of the resulting polymer. This problem was successfully circumvented by the addition of LiCl to the reaction mixture; this compound is known to increase the solvating power of polar aprotic solvents

for various types of polyamides. All the reactions carried out with LiCl in polar aprotic solvents such as HMPA, DMF, DMAc NMP, and DMSO proceeded in solution throughout the polymerization. Thus, KF together with LiCl was found to be a highly efficient catalyst for producing poly(amide-sulfide)s of high inherent viscosities.

Triethylamine was also effective for the base-catalyzed polyaddition of DDT to MBAA, yielding the polymer of high molecular weight. Polymerization with KF–LiCl catalyst progressed rapidly at 60°C and gave reasonably high molecular weight polymer within 1 h. The polyaddition of HDT to MBAA was also successful for the preparation of the polymer with high inherent viscosity, while polymerizations of both PXDT and OBBT with MBAA gave rather inferior results.

The polymers thus formed were identified as linear poly(amide-sulfide)s from their IR spectra and elemental analyses. The IR spectra exhibited an

N-H stretching absorption near 3280 cm^{-1} and a strong carbonyl absorption at $1640\text{--}1630\text{ cm}^{-1}$, with the entire disappearance of absorption at $2560\text{--}2540\text{ cm}^{-1}$ due to thiol groups.

The poly(amide-sulfide)s are soluble in certain acidic solvents like dichloroacetic acid and *m*-cresol at room temperature, and also in hot polar aprotic solvents such as HMPA and NMP. They are insoluble in common organic solvents including benzene, methanol, acetone, and tetrahydrofuran. Films could be cast from *m*-cresol solutions of the polymers having inherent viscosities greater than 0.5 dl g^{-1} . These polymers show no melting points, and begin to decompose at around $280\text{--}300^\circ\text{C}$ in both air and nitrogen atmospheres, as observed by thermogravimetry.

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REFERENCES

1. F. Danusso and P. Ferruti, *Polymer*, **11**, 88 (1970).
2. D. L. Murfin, K. Hayashi, and L. E. Miller, *J. Polym. Sci., A-1*, **8**, 1967 (1970).
3. Y. Imai, M. Ueda, and Y. Sato, *Makromol. Chem.*, accepted.
4. M. Imoto, K. Kondo, and K. Takemoto, *Bull. Chem. Soc. Jpn.*, **37**, 1558 (1964).
5. Y. Minoura and K. Zako, *Kogyo Kagaku Zasshi*, **69**, 340 (1966).
6. E. E. Magat, B. F. Faris, J. E. Reith, and L. F. Salisbury, *J. Am. Chem. Soc.*, **73**, 1028 (1951).
7. Y. Imai, Y. Asamidori, T. Inoue, and M. Ueda, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 583 (1981).
8. I. Belsky, *J. Chem. Soc., Chem. Commun.*, 237 (1977).