SHORT COMMUNICATIONS

Novel Aprotic Polar Polymers IV.
Synthesis of Poly[N-bis(dimethylamino)phosphorylethylenimine] as a Polymer Homolog of Hexamethylphosphoramide

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Poly(2-methyl-2-oxazoline) (PMeOZO) is known as the polymer homolog of an aprotic polar solvent, N,N-dimethylacetamide (DMAc). PMeOZO has high hydrophilicity and good miscibility with polar polymers based on its repeating structure. Thus, PMeOZO is regarded as an aprotic polar polymer.[1] In previous papers, we also prepared the polymers containing sulfoxide groups in repeating structures as novel aprotic polar polymers.[2] They are considered as polymer homologs of dimethyl sulfoxide (DMSO)[3] and actually showed the expected properties such as miscibility with other organic polymers and ability as oxidizing reagents.[2]

Hexamethylphosphoramide (HMPA) is one of the most useful aprotic polar solvents in organic synthesis due to its high polarity and stability to organic and organometallic reagents.[4] HMPA is utilized not only as a solvent but also as an additive or a ligand in organometallic chemistry[5] and as a reagent for changing reaction selectivity.[6] Though HMPA is carcinogenic, it has been widely used because of its usefulness and few alternatives.[7]

Thus, the polymers having HMPA repeating structures can be designed as novel aprotic polar polymers and they are expected to show properties as excellent alternatives of HMPA. The polymers and gels having HMPA structures as substituents on phenyl rings of polystyrene have been prepared and showed good results in some applications,[8] although their versatility as alternatives of HMPA was limited mainly due to their polystyrene main chain. A polymer having HMPA structures in the main chain was also prepared[9] and was found to form polymer complex with poly(methacrylic acid).[10] On the other hand, a polymer possessing bis(dimethylamino)phosphoryl groups as side chains would show better properties as a polymer homolog of HMPA because interaction of phosphoryl groups with other polymers would be easy to occur. In fact, the polymer having sulfinyl groups as side chains showed higher miscibility with other polymers than the main-chain sulfoxide polymers.[2] Therefore, in this paper, we report synthesis and some properties of poly[N-bis(dimethylamino)phosphorylethylenimine] 1, the polymer having phosphoryl groups as side chains, as a polymer homolog of HMPA.


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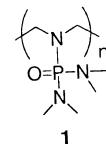
1 as poly(HMPA) was prepared by polymer reaction of linear poly(ethylenimine) with appropriate phosphorylating agent. Linear poly(ethylenimine) was synthesized by alkaline hydrolysis of PMeOZO.[11,12] Poly(ethylenimine) was then converted to poly(HMPA) 1 according to Scheme 1. 1,1,1,3,3,3-Hexamethyldisilazane 3 is known as a silylating agent not to form acidic by-products.[13] Saccharin 4 was used as a catalyst[13] and molecular sieves 4A was added for removing contaminated water and produced ammonia. The resulting poly(HMPA) 1 had 37% phosphoryl units and was obtained in a quantitative yield. The structure of poly(HMPA) was confirmed by ^{1}H NMR and IR spectra and the ratio of introduction of phosphoryl groups was calculated from the integrals of peaks in ^{1}H NMR spectrum (*vide infra*). The number-average molecular weight and the polydispersity index of poly(HMPA) 1 with 37% phosphoryl units were estimated to be 15000 and 1.47 by gel permeation chromatography (GPC).[14] This relative molecular weight is in good agreement with the calculated molecular weight (12000) from the degree of polymerization of PMeOZO.[12] Poly(HMPA) 1 was soluble not only in protic solvents such as water and methanol but also in aprotic polar solvents like acetonitrile and N,N-dimethylformamide and in chloroform and methylene chloride. These results show that poly(HMPA) 1 actually has amphiphilicity expected from its repeating structures.

In order to improve the ratio of introduction of bis(dimethylamino)phosphoryl units, direct reactions of
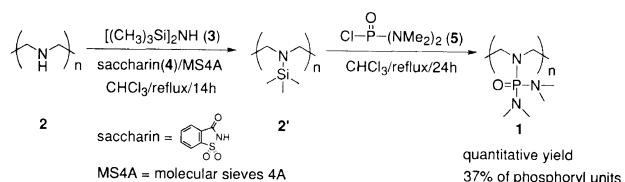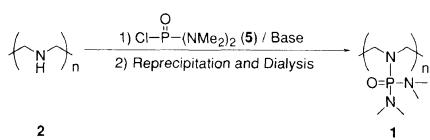

Scheme 1.

Scheme 2.

Table I. Synthesis of poly(HMPA) 1 by direct reaction of poly(ethylenimine) 2 and bis(dimethylamino)phosphoryl chloride 5

Entry	Base	Solvent	Conditions	Results	
				P-Unit[d]/%	Yield/%
1	None	CH_3CN	60°C/36 h	Trace	Quant.
2	TED[a]	CH_3CN	Reflux/37 h	22	Quant.
3	DBU[b]	CH_2Cl_2	Reflux/21 h	29	94
4	DBU[b]	Pyridine	Reflux/19 h	19	40
5	DBU[b]	CH_3CN	60°C/38 h	58	75
6	DBU[b]	DMPU[c]	60°C/41 h	43	89
7	DBU[b]	None	60°C/39 h	44	84

[a] TED = triethylenediamine

[b] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene
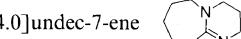
[c] DMPU = N,N'-dimethylpropyleneurea
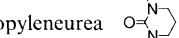
[d] The ratio of introduction of bis(dimethylamino)phosphoryl groups.

poly(ethylenimine) with bis(dimethylamino)phosphoryl chloride in the presence of organic base were examined (Scheme 2). The obtained poly(HMPA) 1 was separated from the salt of organic base by dialysis due to similar solubility of the polymer and the salt. The results of the reactions are summarized in Table I. Polymer with little introduction of bis(dimethylamino)phosphoryl units was obtained when there was no base in the reaction system (entry 1). Triethylenediamine (TED) did not improve the introduction of phosphoryl units (entry 2). On the other hand, as shown in entries 5 and 6, the reactions in aprotic polar solvents such as acetonitrile or N,N'-dimethyl-propyleneurea (DMPU) in the presence of 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) gave poly(HMPA)s having 58 or 43% phosphoryl units, respectively, in good yields. Poly(HMPA) containing 44% phosphoryl units was obtained when the reaction was carried out without any solvent as shown in entry 7. Formation of poly(HMPA) with high introduction of phosphoryl groups would be because of low nucleophilicity of DBU compared with TED.

Figure 1 shows ^{1}H NMR spectrum of poly(HMPA) 1 containing 52% bis(dimethylamino)phosphoryl units. The doublet peak a is assigned to the methyl protons of dimethylamino groups and the peaks for main chain methylene protons b and c are observed as broad peak between 2.9—3.7 ppm. Degree of phosphorylation was calculated from the integrals of these peaks. All amine units in polymer 1 would be quarternarized because the peak for methylene protons adjacent to secondary amine units is usually observed around 2.8 ppm though there is no peak at that position in Figure 1. IR spectrum of poly(HMPA) 1 also supported the presence of HMPA repeating structures and ammonium salts (such as the absorptions at 1636, 1458, 1298, 1197, 1066, 986, and
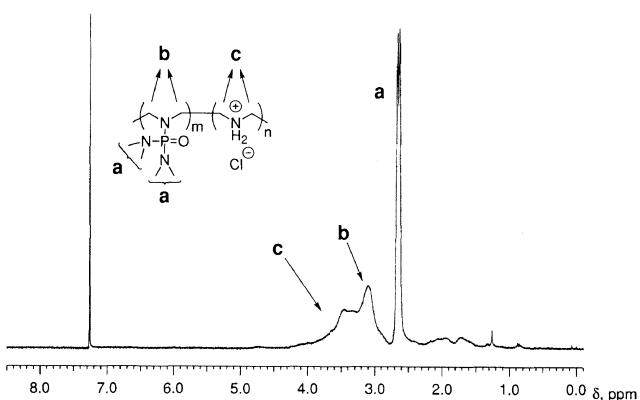
Figure 1. ^{1}H NMR (270 MHz) chart of poly[N-bis(dimethylamino)-phosphorylethylenimine] 1.

Table II. Miscibility of poly(HMPA) 1 with other polymers

Entry	1/wt%[a]	The other polymer/wt%		T_g(s) of the mixture
1	50	50	Poly(2-methyl-2-oxazoline) $M_n = 8500$, $T_g = 71°C$	31, 53°C
2	20	80		42°C
3	80	20		46°C
4	50	50	Poly(N-vinylpyrrolidone) $M_n = 10000$, $T_g = 93°C$	32, 80°C
5	20	80		34, 74°C
6	80	20		33, 59°C
7	50	50	Polystyrene $M_n = 125000$, $T_g = 100°C$	39, 62°C
8	20	80		45, 78°C
9	80	20		51°C

[a] Poly(HMPA) 1 having 47% phosphoryl units was used.

746 cm^{-1}). M_n and M_w/M_n of the polymer having 58% phosphoryl units (Table I, entry 5) estimated from GPC[14] were found to be 15000 and 1.53, respectively, and corresponded to the molecular weight calculated from the degree of polymerization of PMeOZO (14000).[12]

Miscibility of poly(HMPA) 1, which shows the glass transition temperature (T_g) at 30°C, with other organic polymers was examined by differential scanning calorimetry (DSC) method as one of the properties expected in aprotic polar polymers.[2] Samples for DSC analyses were prepared according to ref 15. The resulting samples were subjected to DSC analyses at heating rate of 10°C min^{-1}. The degree of miscibility was estimated by comparing T_gs of the mixture of two polymers with those of the original polymers. Table II summarizes the results of DSC analyses and changes of T_gs were observed in all entries as shown in the table. Especially, only one T_g appeared in entries 2, 3, and 9. Correlation between weight ratio of two polymers and shifts of T_gs is not apparent in these systems, probably because strong interaction derived from polar bis(dimethylamino)-phosphoryl groups exists between two polymers. From these results, it is considered that poly(HMPA) 1 has good miscibility with PMeOZO, poly(N-vinylpyrroli-done), and polystyrene. DSC thermograms of poly-(HMPA) 1, polystyrene and the mixture of these two polymers at a ratio of 80 to 20 are exhibited in Figure 2. From these thermograms, it is obvious that the mix-
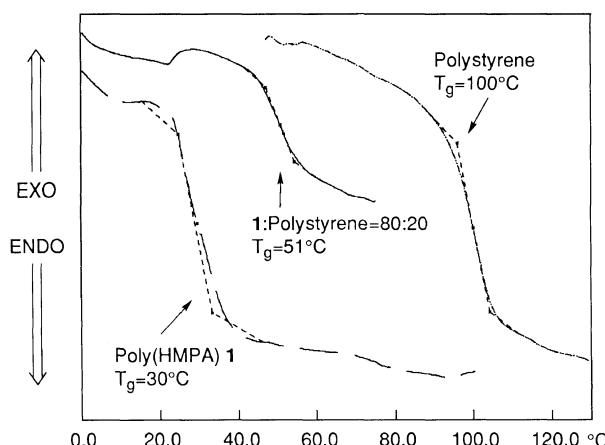
Figure 2. DSC thermograms of poly(HMPA) **1**, polystyrene and the mixture of **1** with polystyrene (80 : 20).

ture of poly(HMPA) **1** with polystyrene has one glass transition temperature, and accordingly that these polymers have good miscibility in this ratio.

In summary, **1** as a novel polymer homolog of HMPA was successfully prepared by polymer reactions of linear poly(ethylenimine) with bis(dimethylamino)phosphoryl chloride. Introduction of phosphoryl units was proved by ^{1}H NMR and IR spectra. Direct reaction of poly-(ethylenimine) with phosphoryl chloride in the presence of DBU gave the poly(HMPA) having bis(dimethyl-amino)phosphoryl units up to 58%. Poly(HMPA) **1** actually showed miscibility not only with PMeOZO and poly(*N*-vinylpyrrolidone) but also with polystyrene. Synthesis of poly(HMPA) having more phosphoryl units by repeating the reactions is currently under way. Examination of miscibility and properties as a polymer solvent and as a polymer additive will be done by using poly(HMPA) possessing 100% phosphoryl units.

REFERENCES AND NOTES

1. T. Saegusa and Y. Chujo, *Makromol. Chem., Macromol. Symp.*, **51**, 1 (1991).

2. (a) T. Oyama, J. Ozaki, and Y. Chujo, *Polym. Bull.*, **37**, 379 (1997). (b) T. Oyama, J. Ozaki, and Y. Chujo, *Polym. Bull.*, **40**, 503 (1998). (c) T. Oyama, J. Ozaki, and Y. Chujo, *Polym. Bull.*, **40**, 615 (1998).
3. R. G. Smith, A. Vanterpool, and H. J. Kulak, *Can. J. Chem.*, **47**, 2015 (1969).
4. For example, in "Fieser and Fieser's Reagents for Organic Synthesis," Vols. 1—16, Wiley, New York, N.Y.
5. J. Inanaga, M. Ishikawa, and M. Yamaguchi, *Chem. Lett.*, 1485 (1987).
6. (a) R. E. Ireland and A. K. Willard, *Tetrahedron Lett.*, 3975 (1975). (b) C. A. Brown and A. Yamaichi, *J. Chem. Soc., Chem. Commun.*, 100 (1979). (c) C. H. Heathcock and D. A. Oare, *J. Org. Chem.*, **50**, 3022 (1985), and references cited therein. (d) J. Lucchetti, W. Dumont, and A. Krief, *Tetrahedron Lett.*, 2695 (1979).
7. Tetrasubstituted ureas such as *N,N'*-tetramethylpropyleneurea (DMPU) were studied and utilized in some reactions as substitutes of HMPA. For example, (a) T. Mukhopadhyay and D. Seebach, *Helv. Chim. Acta*, **65**, 385 (1982). (b) D. Seebach, R. Henning, and T. Mukhopadhyay, *Chem. Ber.*, **115**, 1705 (1982).
8. (a) M. Tomoi, T. Takubo, M. Ikeda, and H. Kakiuchi, *Chem. Lett.*, 473 (1976). (b) S. L. Regen, A. Nigam, and J. J. Besse, *Tetrahedron Lett.*, 2757 (1978). (c) G. Nee, Y. Leroux, and J. Seyden-Penne, *Tetrahedron*, **37**, 1541 (1981). (d) M. Tomoi, T. Hasegawa, M. Ikeda, and H. Kakiuchi, *Bull. Chem. Soc. Jpn.*, **52**, 1653 (1979).
9. A. Bello, W. Bracke, J. Jagur-Grodzinski, G. Sackmann, and M. Szwarc, *Macromolecules*, **3**, 98 (1970).
10. H. Ohno, A. Nii, and E. Tsuchida, *Makromol. Chem.*, **181**, 1227 (1980).
11. T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 108 (1972).
12. Degree of polymerization calculated from ^{1}H NMR spectrum was about 100.
13. C. A. Bruynes and T. K. Jurriens, *J. Org. Chem.*, **47**, 3966 (1982).
14. Eluent: 1,1,1,3,3,3-hexafluoroisopropanol + CF$_3$CO$_2$Na (10 mM). Poly(methyl methacrylate) was used as the standard for calibration.
15. Samples for DSC analyses were prepared as follows: A mixture (0.10 g) of poly(HMPA) **1** with commodity polymer at a desired ratio was dissolved in small amount of chloroform. The solution was then reprecipitated into large amount of *n*-hexane to give a pale yellow solid. After filtration and freeze-drying of the mixture, the resulting solid was dried *in vacuo* and the sample was obtained as a pale yellow powder or gum.