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Synthesis of poly(*N*,*N*-dimethylcarbamoylmethylene) as a polymer homolog of *N*,*N*-dimethylacetamide

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Summary

A novel polymer homolog of *N*,*N*-dimethylacetamide (DMAc) having amide groups on all main chain carbons, poly(*N*,*N*-dimethylcarbamoylmethylene) **1**, was prepared by heating poly(di-*t*-butyl fumarate) **2** at 180 °C for 2 hours followed by treatment with hexamethylphosphoramide at 180 °C for 5 hours. The structure of the obtained polymer **1** was confirmed by ^{1}H-, ^{13}C-NMR and IR spectroscopy. The polymer **1** actually showed the properties based on its repeating structures. **1** had the amphiphilicity and was soluble both in protic and aprotic solvents. Furthermore, **1** showed the miscibility with commodity polymers such as poly(*N*-vinylpyrrolidone), poly(vinyl alcohol) and poly(vinyl chloride). In comparison with another polymer homolog of DMAc, poly(2-methyl-2-oxazoline), the polymer **1** exhibited better miscibility with poly(*N*-vinylpyrrolidone).

Introduction

Aprotic polar solvents are known not only to promote various reactions such as nucleophilic substitution but to show versatile properties such as mixing with water freely and dissolving organic polar polymers. Therefore, many interesting properties based on their repeating structures like the amphiphilicity and the miscibility with other polymers might be expected from polymer homologs of aprotic polar solvents. We have prepared the polymer homologs of dimethyl sulfoxide (DMSO) (1) and hexamethylphosphoramide (HMPA) (2) and it was shown that they actually had the expected properties. On the other hand, poly(2-methyl-2-oxazoline) (PMeOZO) is one of the most famous examples of aprotic polar polymers. This polymer can be regarded as the polymer homolog of *N*,*N*-dimethylacetamide (DMAc) and is known to show the properties such as the miscibility with poly(vinyl chloride), poly(vinylidene fluoride) and the polymers containing amide groups.(3) However, a polymer homolog of DMAc having *N*,*N*-dimethylcarbamoyl groups on all main chain carbons is thought to show better properties than PMeOZO, which is the polymer having nitrogen atoms of amide groups in the main chain (Scheme 1). In fact, the polysulfoxide having sulfoxide groups as side chains exhibited higher miscibility than the polymer containing sulfoxides in the main chain.(1c) Though the polymer **1** was prepared by polymerization of the corresponding monomer (*N*,*N*,*N'*,*N'*-tetramethylfumaramide), the molecular weight of the resulting polymer was not high.(4) In this paper is described the synthesis of poly(*N*,*N*-dimethylcarbamoylmethylene) **1** by the combination of the polymer reactions, that is, the preparation of poly(fumaric acid) by

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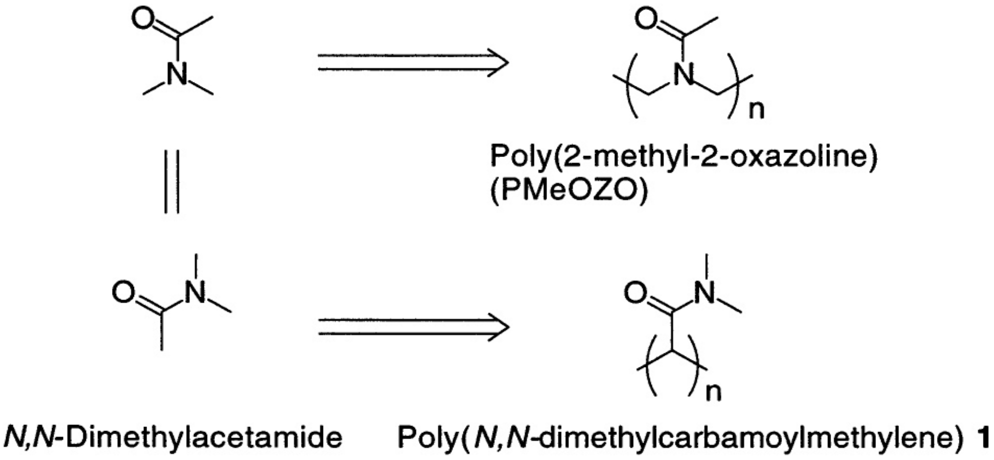
heating poly(di-*t*-butyl fumarate) at 180 °C (5) and the conversion of carboxylic acids to the corresponding *N*,*N*-dimethylamides by heating with HMPA at 180-200 °C.(6) The miscibility of **1** with other organic polymers was also examined.

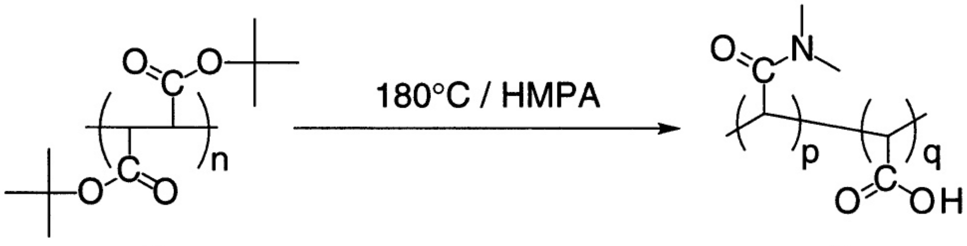
Scheme 1



Results and discussion

Poly(di-*t*-butyl fumarate) **2** as a starting material was prepared by radical polymerization of di-*t*-butyl fumarate (5, 7) using benzoyl peroxide as an initiator according to the literature.(5a) The number average molecular weight and the polydispersity index of the resulting polymer **2** were estimated to be 13000 and 2.6, respectively, by gel permeation chromatography (GPC). The polymer **2** was then subjected to direct reaction with HMPA at 180 °C (Scheme 2). The resulting polymer **1'** is thought to consist of amide and carboxylic acid units from the results of IR spectra. The content of the amide units was calculated by comparing the absorbance of the carbonyl groups of the amide units with that of the carboxylic acid units in IR spectra (*vide infra*), since the determination by ^{1}H-NMR spectroscopy was difficult due to broadening and overlapping of the peaks. A polymer in which most ester groups (81%) were converted to *N*,*N*-dimethylcarbamoyl groups was obtained when the reaction was conducted with one equivalent of HMPA for 8 hours. However, the reproducibility of this reaction was poor possibly because HMPA would prevent the conversion of poly(di-*t*-butyl fumarate) to poly(fumaric acid).

Scheme 2



2 **1'**

Thus, two-step reactions were examined as shown in Scheme 3, which consists of the conversion of **2** to poly(fumaric acid) **3** by heating at 180 °C and subsequent reaction of **3** with HMPA. The results are summarized in Table 1. It became clear that the reaction of the polymer **3** with HMPA for 5 hours afforded poly(*N*,*N*-dimethylcarbamoylmethylene) **1** having almost 100% amide groups (entry 3). The resulting polymer was soluble both in protic solvents such as water and methanol and in aprotic solvents like *N*,*N*-dimethylformamide, acetonitrile, chloroform, dichloromethane and pyridine. These results indicate that poly(*N*,*N*-dimethylcarbamoylmethylene) **1** actually has the amphiphilicity similar to PMeOZO, which is another polymer homolog of DMAc.

Scheme 3

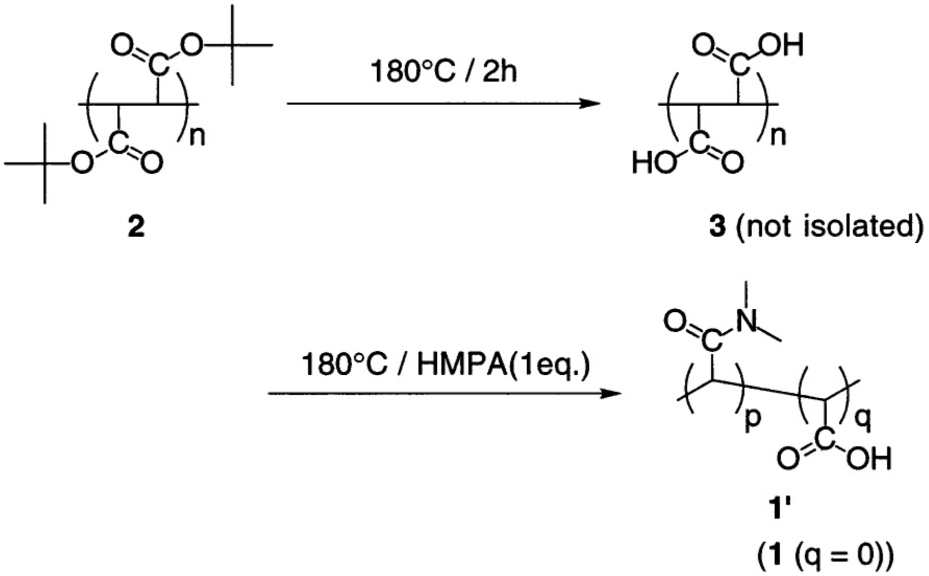
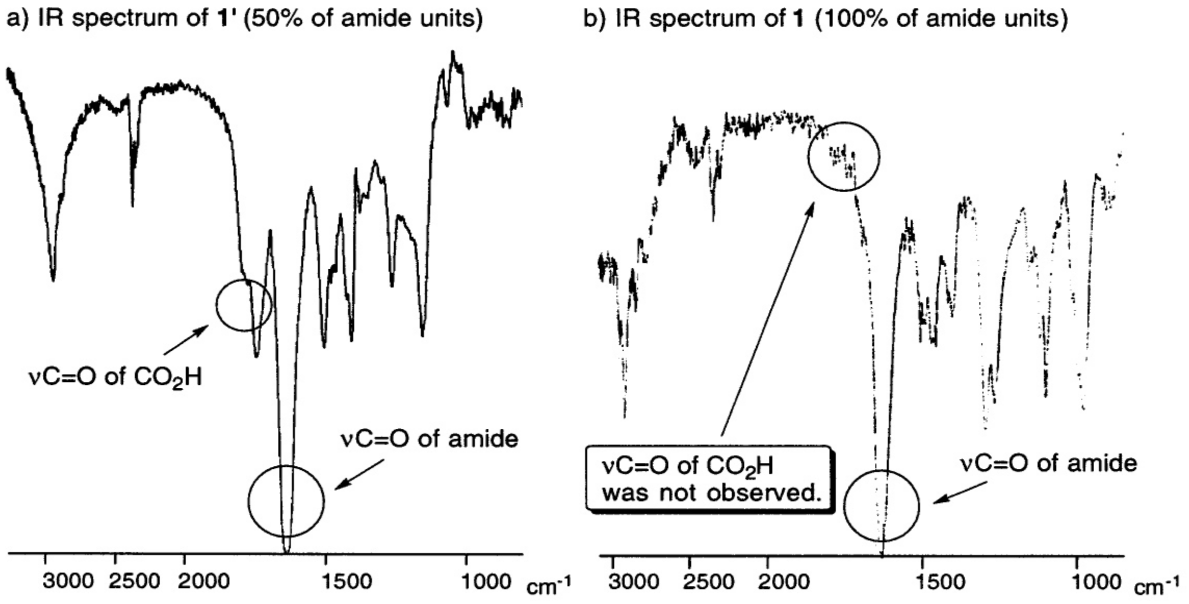


Table 1. Synthesis of the Polymer **1** (or **1'**) by Two-Step Reactions

entry	condition	-C(O)NMe_2 : $\text{-CO}_2\text{H}^a$	yield (%)
1	180 °C, 2+3 h	83 : 17	83
2	180 °C, 2+4 h	78 : 22	51
3	180 °C, 2+5 h	100 : 0	66

[a] The ratio of amide units was calculated from absorptions of νC=O in IR spectra (KBr).

In order to remove contaminated HMPA, the purification of **1** and **1'** was carried out by dialysis of a H_2O solution of the polymers using a cellulose membrane (removing a polymer fraction whose molecular weight is less than 3500). After this procedure, the decrease of the yield of the polymer **1** and **1'** was hardly observed, and therefore, the absolute molecular weight of **1** and **1'** is considered to be much larger than 3500.(8) IR spectra of the polymers in which a ratio of amide units is low (50%) and high (100%, entry 3 in Table 1) are shown in Figures 1a and 1b, respectively. In Figure 1a, absorptions corresponding to the stretching band of the carbonyl groups of carboxylic acid are observed around 1700 cm^{-1} besides an absorption of the amide carbonyl groups at 1640 cm^{-1}. On the other hand, no peak is seen in the region of the C=O stretching band of carboxylic acid in Figure 1b. From these figures, it is obvious that carboxylic acid groups were completely converted to amide groups by two-step reactions as shown in Scheme 3.


a) IR spectrum of **1'** (50% of amide units)

b) IR spectrum of **1** (100% of amide units)

Figure 1. IR spectra (KBr) of the polymer **1'** (a) and **1** (b).

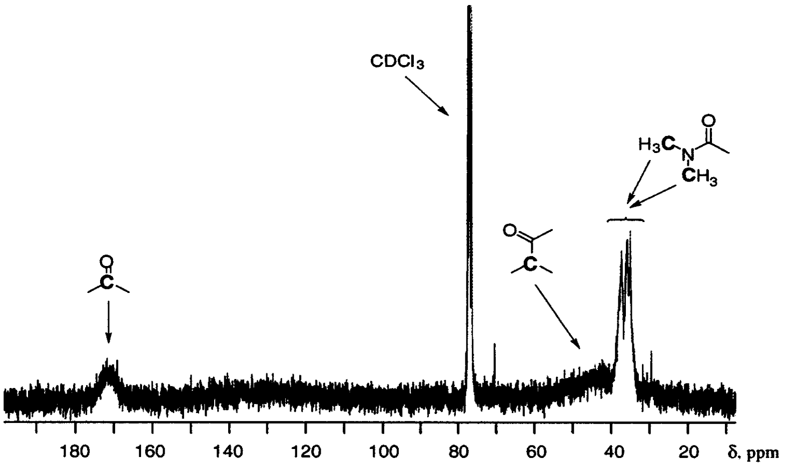


Figure 2. ^{13}C-NMR spectrum (67.9 MHz) of poly(*N,N*-dimethylcarbamoylmethylene) **1**.

Figure 2 depicts ^{13}C-NMR spectrum of the polymer **1**. The peaks corresponding to each carbon of the structure of the polymer were observed at appropriate chemical shifts. ^{1}H-NMR spectrum also supported the structure of the polymer **1**, though the peak broadening and overlapping were observed (see Experimental section).

The miscibility of the polymer **1** (T_g = 18 °C) with other organic polymers was examined as one of the expected properties of aprotic polar polymers.(1-3) The degree of miscibility was estimated by comparing the glass transition temperatures (T_gs) of the mixture with those of the original polymers by using differential scanning calorimetry (DSC) method at heating rate of 10°C / min. The samples for DSC analyses were prepared as described in Experimental Section.

The results are summarized in Table 2, and shifts of the glass transition temperatures were observed in the systems of **1** with poly(*N*-vinylpyrrolidone) (PVP), poly(vinyl alcohol) and poly(vinyl chloride). Especially, when the ratio of **1** to PVP was 80:20, one T_g was observed between those of the original polymers (entry 3). These results indicate that the polymer **1** actually has good miscibility with other polymers and that **1** can be regarded as a novel aprotic polar polymer. The ratio of two polymers did not necessarily correspond to the shift of the glass transition temperatures in these systems. This would suggest the presence of strong interaction derived from polar amide groups of the polymer **1**.

Table 2 . Miscibility of **1** (T_g = 18 °C) with Other Polymers

entry	**1** (wt%)	the other polymer (wt%)		T_gs (°C)
1	50	50	Poly(*N*-vinylpyrrolidone) M_n = 10000, T_g = 93 °C	25, 68
2	20	80		28, 94
3	80	20		26
4	50	50	Poly(vinyl alcohol) M_n = 10000, T_g = 85 °C	46, 65
5	20	80		42, 67
6	80	20		38, 52
7	50	50	Poly(styrene) M_n = 125000, T_g = 97 °C	26, 93
8	20	80		-[a]
9	80	20		28, 91
10	50	50	Poly(vinyl chloride) M_n = 31000, T_g = 77 °C	47, 59
11	20	80		31, 55
12	80	20		28, 60

[a] The mixture was macroscopically separated.

Table 3 . Miscibility of Polymer homologs of DMAc with PVP

entry	poly(DMAc) (wt%)		PVP[a] (T_g = 93°C) (wt%)	T_gs of blend (°C)
1	50	**1** (T_g = 18°C)	50	25, 68
2	20		80	28, 94
3	80		20	26
4	50	PMeOZO[b] (T_g = 71°C)	50	63, 103
5	20		80	84, 92
6	80		20	64, 96

[a] M_n = 10000.
[b] M_n = 8500.

Then, the miscibility of the polymer **1** with PVP was compared with the miscibility of PMeOZO with PVP. Table 3 summarizes the results, and one T_g was observed when a ratio of the polymer **1** with PVP was 80:20 as shown in entry 3. On the other hand, the mixtures of PMeOZO with PVP showed two T_gs at all ratios (entries 4-6). Thus, the miscibility of the polymer **1** with PVP is thought to be better than that of PMeOZO with PVP, and **1** is regarded as a novel type of polymer homolog of DMAc. The difference in the miscibility between **1** and PMeOZO would be derived from the functionalized polymethylene structure of **1**.

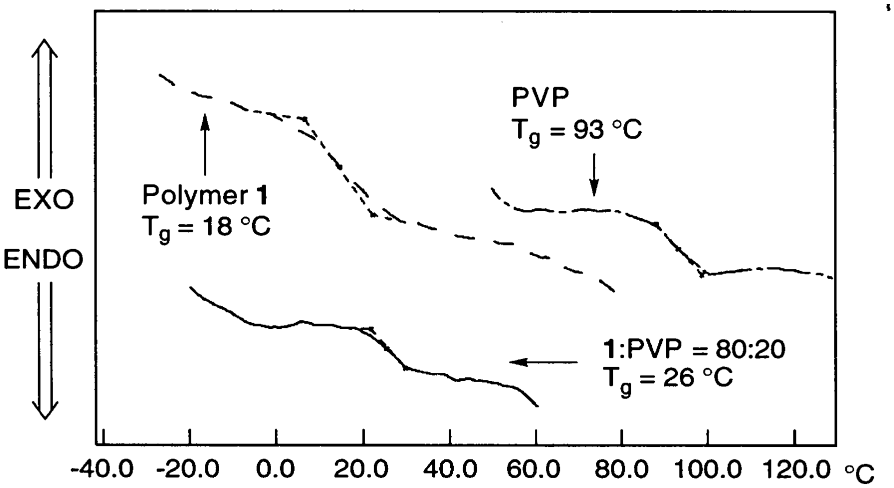


Figure 3. DSC thermograms of the polymer **1**, PVP, and 80:20 mixture of these polymers.

DSC thermograms of the polymer **1**, PVP and 80:20 mixture of these polymers are shown in Figure 3. In fact, one T_g is observed between those of the original polymers in the DSC thermogram of the mixture.

Conclusion

Poly(*N*,*N*-dimethylcarbamoylmethylene) **1** was successfully prepared by heating poly(di-*t*-butyl fumarate) at 180 °C for 2 hours followed by treatment with HMPA for 5 hours. Almost quantitative introduction of amide units was confirmed by IR, ^{1}H- and ^{13}C-NMR spectroscopy. The polymer **1** was found to be amphiphilic and to have good miscibility with PVP, poly(vinyl alcohol) and poly(vinyl chloride). The miscibility of **1** with PVP was found to be better than that of PMeOZO with PVP. We are currently investigating milder methods to prepare the polymer **1** and application of the polymer reaction strategy to the synthesis of other polymers having functional groups on all main chain carbons.

Experimental section

General. ^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz for ^{1}H-NMR and 67.9 MHz for ^{13}C-NMR) in chloroform-*d*. IR spectra were recorded on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses (GPC) were carried out by using chloroform as an eluent on a Tosoh UV-8011 and RI-8000 (Shodex K-803L column) after calibration with standard polystyrene. GPC analyses with water and methanol (1:1) + NaCl (10 mM) as an eluent were conducted on a Tosoh RI-8010 (TSKgel G5000PW column) after calibration with standard poly(ethylene oxide). All DSC analyses were carried out on a Seiko DSC200 instrument by using about 10 mg of exactly weighed samples at heating and cooling rate of 10 °C / min. Dialysis was conducted with a cellulose membrane purchased from Nacalai

Tesque, Inc. (Cellulose Dialyzer Tubing VT351) for removing a polymer whose molecular weight was less than 3500.

Unless otherwise noted, the materials were obtained from commercial sources and used after distillation under nitrogen. *t*-Butanol and HMPA were distilled under nitrogen from CaH_2. Benzoyl peroxide was recrystallized by adding methanol into its chloroform solution. Potassium *t*-butoxide was purchased from Nacalai Tesque, Inc. and used as received. PVP, polystyrene and poly(vinyl chloride) were obtained from commercial sources and used without further purification. Poly(vinyl alcohol) was used after reprecipitation into acetone. PMeOZO was prepared by ring-opening polymerization of 2-methyl-2-oxazoline as described in reference 3.

Synthesis of di-*t*-butyl fumarate. To a 95 ml *t*-butanol suspension of potassium *t*-butoxide (10.4 g, 92.5 mmol) was added dropwise fumaryl chloride (5.0 ml, 46.3 mmol). After starting addition, an exothermic reaction occurred and further addition was continued at such a rate that the reaction temperature did not exceed 50 °C. The mixture was then refluxed for 4 hours. After cooling, the dark brown solution was poured into water and extracted with diethyl ether twice, and water layer was then washed by diethyl ether twice. The organic layers were collected, dried with anhydrous $MgSO_4$ and evaporated. The resulting solid was purified by recrystallization from isopropanol and sublimation at 68 °C under 0.42 miHg to give white crystals in 35% yield. ^{1}H-NMR(δ, ppm) 1.49 (-C$(CH_3)_3$, S, 18H), 6.66 (=CH-, s, 2H); ^{13}C-NMR(δ, ppm) 28.0, 81.6, 134.6, 164.4.

Synthesis of poly(di-*t*-butyl fumarate) 2. In a test tube were placed di-*t*-butyl fumarate (2.80 g, 12.3 mmol) and benzoyl peroxide (13.4 mg, 0.45 mo of the monomer) as a radical initiator. The test tube was then sealed and heated at 80 °C for 19 hours. After polymerization, the content of the tube was dissolved in toluene and poured into a large amount of methanol to give a white solid. The resulting solid was filtered and dried under reduced pressure for 6 hours to afford **2** in 80% yield. ^{1}H-NMR(δ, ppm) 1. 00-1.90 (-C$(CH_3)_3$, br, 18H), 2.42-3.92 (-CH-, br, 2H); ^{13}C-NNM(δ, ppm) 28.6, 43.0-50.0, 81.0, 169.2; IR(KBr) 2982, 2937, 1729, 1147 cm^{-1}. The value of molecular weight was given in Results and Discussion.

Direct reaction of poly(di-*t*-butyl fumarate) 2 with HMPA. General procedure. In a two-necked test tube equipped with a reflux condenser were placed poly(di-*t*-butyl fumarate) **2** (0.15 g, 1.31 mmol of carbonyl groups) and an appropriate amount of HMPA (one or twenty equivalents). The mixture was then heated at 180 °C for desired time (3.5-11 hours). It is important that the reaction temperature should be maintained at 175-185 °C for the progress of the reaction without decomposition of the polymer. To the resulting mixture was added 5 ml of chloroform and the solution was poured into a large amount of diethyl ether. A dark brown solid was collected by suction filtration, dissolved in water and purified by dialysis exchanging external water 4-5 times in every 5 hours to give the polymer **1'** having 58-81% amide units. The ratio of amide units to carboxylic acid units was calculated from the ratio of the absorbance of C=O stretching band of amide groups with that of carboxylic acid groups by using 1: 1 mixture of *N*,*N*-dimethylacetamide with acetic acid as a standard for calibration. ^{1}H-NMR(δ, ppm)

2.92 (-NCH_3, br), 4.80 (-CH-, br, 1H); IR(KBr) 2931, 1741, 1636, 1498, 1402, 1149 cm^{-1}.

Synthesis of poly (*N*,*N*-dimethylcarbamoylmethylene) 1. In a two-necked test tube equipped with a reflux condenser was placed poly(di-*t*-butyl fumarate) **2** (0.15 g, 1.31 mmol of carbonyl groups). After **2** was heated at 180 °C for 2 hours, one equivalent of HMPA (0.228 ml, 1.31 mmol) was added and the content was heated at 180 °C for 5 hours. As mentioned above, it is crucial that the reaction system is kept at 175-185 °C to prevent degradation of the polymer and to promote the reaction. The work-up and the purification of the resulting polymer were carried out by the procedure described above and the polymer **1**, in which no carboxy group was observed by IR spectrum, was obtained in 66% yield. ^{1}H-NMR(δ, ppm) 2.92 (-NCH_3, br, 6H), 4.80 (-CH-, br, 1H); ^{13}C-NMR(δ, ppm) 36.3, 37.5, 42.2 (br), 171.8; IR(KBr) 2926, 1636, 1469, 1402 cm^{-1}. The value of molecular weight was given in Results and discussion.

Differential scanning calorimetry analyses. The samples for DSC analyses were prepared as follows: A mixture (0.10 g) of **1** or PMeOZO with a commodity polymer at a desired ratio was dissolved in a small amount of chloroform (mixtures with PVP and with polystyrene), water (a mixture with poly(vinyl alcohol)) or *N*,*N*-dimethylformamide at 60 °C (a mixture with poly(vinyl chloride)). The solution was then reprecipitated into a large amount of *n*-hexane (PVP), diethyl ether (polystyrene and poly(vinyl chloride)) or THF (poly(vinyl alcohol)) to give a brown solid. After filtration and freeze-drying of the mixture, the resulting solid was dried *in vacuo* and used for DSC analyses. The midpoint of T_g peak in the thermogram of the second heating scan was adopted as the value of the glass transition temperature.

References and notes

1. (a) Oyama T, Ozaki J, Chujo Y (1997) Polym Bull 37: 379. (b) Oyama T, Ozaki J, Chujo Y (1998) Polym Bull 40: 503. (c) Oyama T, Ozaki J, Chujo Y (1998) Polym Bull 40: 615. (d) Oyama T, Naka K, Chujo Y, Macromolecules submitted.
2. (a) Oyama T, Ohkubo Y, Naka K, Chujo Y (1998) Polym J 30: 1008. (b) Oyama T, Ohkubo Y, Naka K, Chujo Y (1999) Polymn J in press.
3. Saegusa T, Chujo Y (1991) Makromol Chem, Macromol Symp 51: 1, and references cited therein.
4. Matsumoto A, Fukushima K, Otsu T (1991) J Polym Sci Part A: Polym Chem 29: 1697.
5. (a) Otsu T, Yasuhara T, Shiraishi K, Mori S (1984) Polym Bull 12: 449. (b) Otsu T, Yasuhara T, Matsumoto A (1988) J Mocromol Sci-Chem A25: 537. (c) Kitano T, Ishigaki A, Uematsu G, Kawaguchi S, Ito K (1987) J Polym Sci Part A: Polym Chem 25: 979.
6. Kopecky J, Smejkal J (1966) Chemistry and Industry 1529.
7. Crivello JV, Shim S-Y (1995) J Polym Sci Part A: Polym Chem 33: 513.
8. M_n = 3300 and M_w / M_n = 1.94 in GPC (eluent: water and methanol (1:1) + NaCl (10 mM)). Poly(ethylene oxide) was used as the standard for calibration.