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Anionic Synthesis of Narrow Molecular Weight Distribution Water-Soluble Poly(*N*,*N*-dimethylacrylamide) and Poly(*N*-acryloyl-*N*′-methylpiperazine)

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ABSTRACT: Water-soluble poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(*N*-acryloyl-*N*′-methylpiperazine (PAMP) were prepared in tetrahydrofuran at −78 °C by anionic polymerization in the presence of monofunctional initiators such as (triphenylmethyl)lithium, or -cesium or the difunctional initiators (1,1,4,4-tetraphenylbutyl)lithium, -potassium, or -cesium or cesium naphthalenide. Polymerizations initiated especially in the presence of cesium as counterion proceeded in a homogeneous manner and gave polymers having controlled molecular weights and narrow molecular weight distributions in quantitative yields. However, the polymerization results in polymers with a lower molecular weight and a broad molecular weight distribution at higher reaction temperatures. Size exclusion chromatography, ^{1}H NMR spectroscopy, and intrinsic viscosity measurements support the clean anionic polymerization of DMA with few side reactions at −78 °C. Attempted anionic polymerizations of methacrylamide monomers such as *N*,*N*-dimethylmethacrylamide and *N*-methacryloyl-*N*′-methylpiperazine are described as well. NMR spectroscopy, differential scanning calorimetry, and solubilities of the resulting polymers revealed the influence of the initiator counterions on the polymer tacticity.

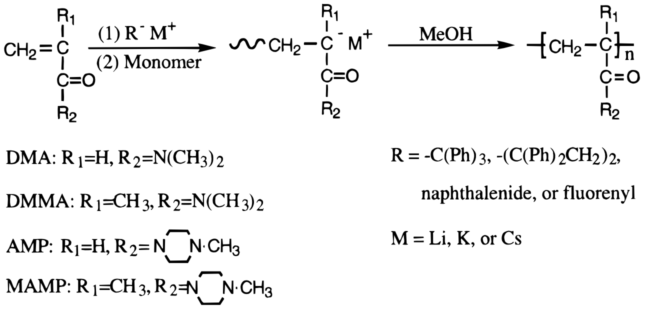
Introduction

Anionic "living" polymerizations proceed with the absence of chain transfer and termination reactions on the polymerization time scale and are very useful in the synthesis of narrow molecular weight distribution polymers, block copolymers, and polymers with unusual architectures.[1−6] Living polymerization techniques have been applied to the synthesis of well-defined water-soluble polymers. Examples are polyelectrolytes prepared by anionic polymerizations of hydrophobic monomers such as styrene, 4-vinylpyridine, or *tert*-butyl acrylate and followed by sulfonation,[7] quaternization,[8] or hydrolysis,[9] respectively. Nonionic associating water-soluble polymers can be made by anionic polymerization of ethylene oxide followed by end functionalization with hydrophobic groups.[10,11]

We recently reported the synthesis of perfluorocarbon-containing water-soluble polymers such as polyacrylamides (PAMs) and perfluorocarbon derivatives of hydroxyethyl cellulose (HEC).[12,13] Such polymers, particularly the PAMs, were shown to be extremely effective viscosifiers compared to the corresponding hydrocarbon analogues. The PAM copolymers were synthesized by radical copolymerization of the water-soluble vinyl monomer acrylamide and hydrophobic perfluoroalkyl-containing acrylates. Such polymers are polydisperse and not well defined with regard to comonomer sequence. As a result, the synthesis of narrow molecular weight distribution nonionic water-soluble polymers that are well defined with regard to the number and placement of hydrophobic groups is of considerable interest.

Although polyacrylamides of this type cannot be synthesized by living, i.e., anionic polymerization, the anionic polymerization of water-soluble *N*,*N*-disubstituted acrylamides is known.[14a] We now report the first successful synthesis of monodisperse well-defined poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(*N*-acryloyl-*N*′-methylpiperazine) (PAMP) by anionic polymerization. The synthesis of such polymers is a prerequisite for the synthesis of the corresponding telechelic polymers containing hydrophobic end groups that are of interest in studies of the role of hydrophobe placement in hydrophobic association.

Scheme 1



The free-radical polymerizations of *N*,*N*-dimethylacrylamide (DMA) and *N*-acryl-*N*′-methylpiperazine (AMP) were reported in previous publications.[14−18] The structure, stereochemistry, and thermal properties of PDMA have been studied by several groups[14−16] by X-ray, by DSC, and by ^{1}H and ^{13}C NMR. PAMP has been synthesized by Ferruti et al.[17] and Li et al.[18] using free-radical techniques. This polymer may be converted to a cationic polyelectrolyte by quaternization. In addition, this polymer may have interesting properties as a biocompatible material.[19]

The present paper describes the anionic polymerization of DMA and AMP in tetrahydrofuran (THF) at −78 °C to give narrow molecular weight distribution PDMA and PAMP (Scheme 1)

Experimental Section

Reagents and Solvents. 1,1-Diphenylethylene (DPE) was first purified by fractional distillation and then distilled from a potassium mirror under vacuum. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was purified by distillation over calcium hydride. THF received from Mallinckrodt (AR grade) was dried and distilled from sodium/potassium alloy.

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Initiators. Alkyllithiums (*n*-butyl, *sec*-butyl, *tert*-butyl) were purchased from Aldrich and used as received. (Triphenylmethyl)lithium (TPM-Li) and -cesium (TPM-Cs) were prepared by the reaction of triphenylmethane with the alkali metals in THF at room temperature. The initiators (1,1,4,4-tetraphenylbutyl)lithium (TPB-Li_2), -potassium (TPB-K_2), and -cesium (TPB-Cs_2) salts were prepared by addition of the corresponding alkali metals to purified DPE dissolved in THF. Cesium naphthalenide (NapCs) was prepared by the reaction of a small excess of naphthalene with cesium metal in THF at room temperature. Fluorenylcesium (FlCs) was prepared by the deprotonation of fluorene with TPB-Cs_2 in THF. After filtration, all carbanion solutions were sealed into evacuated ampules equipped with breakseals and stored in a freezer. The concentrations of initiators were determined by conventional acid/base titration or by UV/visible spectroscopy.[20]

***N,N*-Dimethylacrylamide (DMA).** DMA purchased from Aldrich Chemical Co., Inc. was distilled under vacuum over finely crushed calcium hydride. The fraction collected at 35−38 °C was further distilled over calcium hydride on the high-vacuum line (~10^{-6} mmHg), and sealed into ampules before use. Proton NMR (CD_3OD) (ppm): δ 2.99 (s, 3H, cis CH_3), 3.13 (s, 3H, trans CH_3), 5.69−5.74 (q, 1H, trans β-H), 6.15−6.23 (q, 1H, cis β-H), 6.69−6.80 (q, 1H, α-H). ^{13}C NMR (CD_3OD): δ 35.9 (cis NCH_3), 37.8 (trans NCH_3), 128.2 (vinyl, $CH_2{=}$), 129.0 (vinyl, $={CH}$), 168.6 (carbonyl, $C{=}O$).

***N,N*-Dimethylmethacrylamide (DMMA).** DMMA (Polysciences Inc.) was purified using the same procedures for DMA. The fraction collected at 45−48 °C at reduced pressure. The purified monomer was stored in evacuated ampules. ^1H NMR (CD_3OD) (ppm): δ 1.92 (s, 3H, α-CH_3), 2.96 (s, 3H, cis CH_3), 3.07 (s, 3H, trans CH_3), 5.02−5.03 (d, 1H, cis β-H), 5.23−5.24 (d, 1H, trans β-H). ^{13}C NMR (CD_3OD): δ 20.3 (α-CH_3), 34.9 (cis NCH_3), 39.2 (trans NCH_3), 116.5 (vinyl, $CH_2{=}$), 142.0 (vinyl, $={C}$), 173.5 (carbonyl, $C{=}O$).

***N*-Acryl-*N*′-methylpiperazine (AMP).** Freshly distilled acryloyl chloride (Aldrich; 116 g, 1.284 mol) in 100 mL of methylene chloride was added dropwise into a rapidly stirred solution of 1-methylpiperazine (Aldrich; 86 g, 0.856 mol) in dry methylene chloride (400 mL) with cooling in an ice/salt bath. After the addition, the reaction mixture was stirred at ambient temperature for 15 h in order to ensure complete conversion. The yellowish precipitated HCl salt was filtered from the reaction solution and was neutralized by addition of excess sodium hydroxide solution (0.5 M). The mixture was extracted five times by methylene chloride (50 mL). The organic layer and the filtrate from the previous step were combined and concentrated in a rotary evaporator. The crude product was distilled under vacuum and yielded 80 g (60%) of a colorless liquid by collecting the fraction at 82−92 °C under a reduced pressure. The AMP was further dried and purified by repeated distillation over calcium hydride. The purity of the monomer analyzed by capillary gas chromatography is greater than 99.9%. ^1H NMR (CD_3OD) (ppm): δ 2.30 (s, 3H, CH_3), 2.42−2.46 (t, 4H, CH_2), 3.63−3.67 (m, 4H, CH_2), 5.71−5.76 (q, 1H, trans β-H), 6.16−6.23 (q, 1H, cis β-H), 6.71−6.81 (q, 1H, α-H). ^{13}C NMR (CD_3OD): δ 42.7 (cis NCH_2), 46.0 ($N'CH_3$), 46.4 (trans NCH_2), 55.5 (cis $N'CH_2$), 56.1 (trans $N'CH_2$), 128.7 (vinyl, $CH_2{=}$), 128.8 (vinyl, $={CH}$), 167.3 (carbonyl, $C{=}O$).

***N*-Methacryloyl-*N*′-methylpiperazine (MAMP).** The same procedure was followed as described above instead of using methacryloyl chloride (92 g, 0.88 mol) and 1-methylpiperazine (77 g, 0.77 mol). Distillation at 100−114 °C (1 mmHg) gave 85 g of a colorless liquid in 66% yield. ^1H NMR (CD_3OD) (ppm): δ 1.95−1.95 (q, 3H, α-CH_3), 2.31 (s, 3H, CH_3), 2.38−2.40 (t, 4H, CH_2), 3.60 (s, 4H, CH_2), 5.02−5.03 (q, 1H, cis β-H), 5.17−5.19 (q, 1H, trans β-H). ^{13}C NMR (CD_3OD): δ 20.5 (α-CH_3), 42.2 (cis NCH_2), 46.0 ($N'CH_3$), 47.8 (trans NCH_2), 55.5 (cis $N'CH_2$), 56.2 (trans $N'CH_2$), 116.6 (vinyl, $CH_2{=}$), 141.5 (vinyl, $={CH}$), 173.0 (carbonyl, $C{=}O$).

Polymerizations. All anionic polymerizations were carried out under high vacuum (10^{-5}−10^{-6} mmHg) conditions in an all-glass apparatus (500 mL). The reaction apparatus equipped with reagent ampules and a side bulb was evacuated and dried with a low-temperature flame prior to addition of a carbanion washing solution. A certain amount of THF dried over Na/K alloy was distilled through the vacuum line into the vessel. The vessel was rinsed with the carbanion solution that was then poured back to the side bulb from which THF was again distilled into the reaction vessel. After repeating this procedure several times, the required quantity of initiator solution was introduced into the vessel which was then cooled to the desired temperature. The monomer (1−2 g) was added into the stirred initiator solution by distillation or by direct addition from an ampule. The reaction solution was stirred for 30 min followed by addition of methanol to terminate the polymerization. The vessel was then opened to the air, and 2 mL of the reaction solution was collected for size exclusion chromatography (SEC) analysis without further purification. The polymer was precipitated by dropwise addition of the reaction mixture to an excess of hexane and then dried in a vacuum oven at 50 °C for 48 h.

In order to evaluate the relationship between the tacticity and solubility of the polymers, radical polymerizations of DMA, DMMA, AMP, or MAMP were also performed. Into a single-neck round-bottom flask (50 mL) capped with a rubber septum and containing a Teflon magnetic stirrer was loaded 2 g of monomer dissolved in 18 mL of deionized water. A stream of ultrapure grade argon (Phoenix Distributors) was bubbled through the flask for 30 min in order to remove oxygen and other impurities. Aqueous solutions containing 0.95 mg of $(NH_4)_2S_2O_8$ and 1.15 mg of $Na_2S_2O_5$ in 0.5 mL as a redox initiator were injected with a syringe through the rubber septum into the rapidly stirred contents of the flask. The reaction was continued at 50 °C for 24 h. The polymer was isolated by pouring the reaction solution into cold acetone and was dried in vacuo at 50 °C for 48 h.

Characterization. Molecular weight and molecular weight distributions were obtained by SEC (Waters) equipped with refractive index and ultraviolet detectors, using two Ultra-μ-styragel columns (500, 10 000 Å) at a flow rate of 1.0 mL/min in THF at 25 °C and using polystyrene standards.

The ^1H and ^{13}C NMR spectra were obtained with 5% $CDCl_3$ or CD_3OD solution at 30 °C using a Bruker AM-360 spectrometer operating at 360 and 90 MHz, respectively. The chemical shifts in ppm are referenced to tetramethylsilane (TMS) internal standard. The IR spectra were obtained using an IBM FTIR spectrophotometer, on NaCl crystal disks for liquid monomers or KBr pellets (1 wt %) for solid polymers. The glass transition temperatures (T_g) of the polymers were determined by the use of Perkin-Elmer DSC-7 system with a heating rate of 20 °C/min under an argon atmosphere. The midpoint of the abrupt heat-capacity jump during the second run was taken as T_g. Modified neglect of diatomic overlap (MNDO) calculations were performed on an IBM Power Station 560 using a Spartan Electronic Structure Program.

Results and Discussion

Anionic Polymerizations of DMA and AMP. Anionic polymerization of DMA and AMP was carried out in THF at −78 °C with various initiators such as alkyllithiums (*n*-butyl, *sec*-butyl, *tert*-butyl), (triphenylmethyl)lithium and -cesium, (1,1,4,4-tetraphenylbutyl)dilithium, -dipotassium, and -dicesium, and cesium naphthalenide. The polymerizations proceeded in a heterogeneous or homogeneous manner, depending on the counterions. In the presence of Li^+, the polymer precipitated out during polymerization. This was apparently due to a lack of polymer solubility since the precipitate remained after termination by MeOH. Thus, the precipitation was not caused by aggregation of the PDMA carbanion lithium salt. With increasing cation size, the solubility of the polymer increased. With K^+ as a counterion, the solubility of the polymer was found to be greater, and in the presence of Cs^+ counterion, a completely homogeneous reaction system was obtained. Thus, most polymerizations were carried out using Cs^+ salts as initiators.

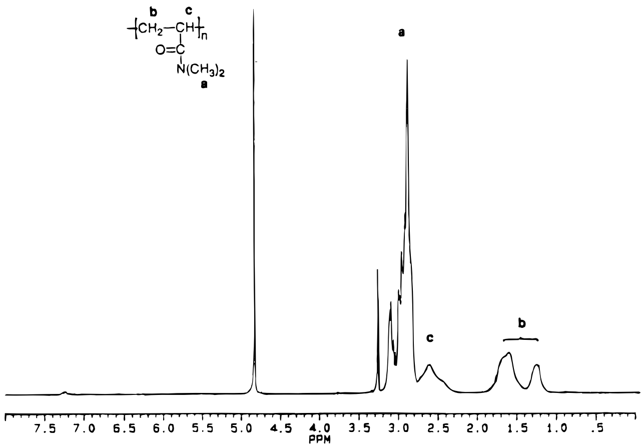


Figure 1. Typical 360 MHz ^{1}H NMR spectrum of PDMA (Table 1, run 5) in CD_3OD at 30 °C.

The polymerization in all cases proceeded rapidly (<5 min) at −78 °C whether the reaction system was heterogeneous or homogeneous. Initiation in all cases was instantaneous as judged by a rapid color change from the red (TPM^-, M^+ or TPB^{2-}, $2M^+$) or green (NapCs) solutions to a slightly yellowish or colorless solution. Monomer conversions were determined by withdrawal of an aliquot of the reaction solution from the reaction vessel 5 min after monomer addition. Analysis by SEC indicated that all polymerizations were completed within 5 min at −78 °C. In contrast with TPM-Cs, TPB-Cs_2, or NapCs, fluorenyl cesium (FlCs) did not initiate the polymerization of DMA, probably due to the relatively low basicity of fluorenyl anion. The orange color of the initiator solution remained unchanged, indicating that the initiation by fluorenyl salts is slow or nonexistent. This is attributable to the large difference in basicity between the fluorenyl (pK_a of fluorene, 23) and di- or triphenyl methanyl anion (pK_a of triphenylmethane, 32−36).

The ^{1}H NMR spectrum of PDMA (Figure 1) shows the absence of vinyl protons and the presence of methylene and methine protons. The $N(CH_3)_2$ group shows a resonance at 2.8−3.2 ppm, the CH proton absorbs at 2.3−2.7 ppm, and CH_2 protons absorb at 1.2 and 1.7 ppm. Interestingly, two methylene resonances were observed in $CDCl_3$ or CD_3OD. Similar results were obtained by Gia and McGrath.[15a,b] The ^{13}C NMR spectra also show the absence of the vinyl carbons, the other signals remaining roughly in the same regions in the monomer and polymer spectra. The infrared spectrum of the polymer showed a strong absorption of the amide carbonyl group at 1636 cm^{-1}, whereas that of the monomer was observed at 1614 cm^{-1}.

The molecular weights and molecular weight distributions were determined by SEC based on polystyrene standards. For low molecular weight PDMAs, the number-average molecular weights (M_n) could be determined in CD_3OD by ^{1}H NMR integration of the aromatic protons of the initiator fragment observed at ~7.3 ppm relative to the methylene and methine protons of the polymer chain. The results of the polymerizations are summarized in Table 1. The molecular weights of low molecular weight PDMA measured by NMR and SEC, and those calculated from the molar ratios of monomer to initiator, were observed to be in good agreement. However, for higher molecular weights ($M_n \geq 10\,000$), significant discrepancies were found between the PDMA molecular weights measured by NMR and those determined by SEC or by calculation (Table 1). This greater deviation probably is due to an NMR integration error. The viscosity-average molecular weights M_v obtained from viscosity measurements were found to be of the same order of magnitude as the M_w's calculated from SEC measurements.

The polydispersities of the resulting polymers range from 1.06 to 1.86, depending on conditions. Most PDMA molecular weight distributions were narrow, indicating that the polymerizations occurred with few side reactions. TPM-Cs in THF at −78 °C generated the narrowest (MWD) polymers (MWD < 1.10). The bifunctional initiator (TPB-Cs_2) and NapCs also gave narrow distributions for relatively low molecular weights, but the distributions became broader for very high molecular weights (MW > 190 000). In one case, a broad MWD polymer (Table 1 run 10) was obtained as a result of inadvertent thermal polymerization in the purified monomer. This was avoided by addition of the monomer via distillation or by addition of a THF solution containing freshly distilled monomer.

From the above results, the anionic polymerization of DMA at −78 °C appears to proceed without transfer and termination reactions. In order to further explore the living character of the polymerization system at −78 °C, a two-stage polymerization of DMA was carried out by addition of second portion of monomer 20 min after initiation of DMA by TPM-Cs. The second-stage polymerization proceeded quantitatively to produce a polymer with the calculated molecular weight and narrow MWD as listed in Table 1 (run 17). This indicates that the propagating DMA carbanion at −78 °C under these conditions does not undergo side reactions. Cesium naphthalenide initiators give similar results (Table 1, run 18). The appreciable kinetic stability of amide anions was reported by Woodbury and Rathke,[21] who prepared α-lithium−*N*,*N*-dimethylacetamide in THF at 0 °C and found only a small amount of the condensation product of *N*,*N*-dimethylacetamide after 60 h at 25 °C.

Polymerizations of DMA (Table 1, runs 2 and 5) were carried out at 0 and −78 °C but with similar concentrations of initiator and monomer. The polymerization (Table 1, run 2) at 0 °C produced a much broader MWD polymer (MWD = 1.86) than the one produced at −78 °C (MWD = 1.07), as shown in Figure 2. The SEC chromatogram of the polymer prepared at 0 °C showed a pronounced low molecular weight tail and the M_n of 9500 obtained was much lower than the calculated M_n (16 000), indicating the occurrence of chain transfer.

The polymerizations of AMP also proceeded in a homogeneous manner in the presence of Cs^+ counterions and gave polymers having controlled molecular weights and relatively narrow molecular weight distributions in quantitative yields, as shown in Table 2. The formation of PAMP was indicated by ^{1}H NMR spectrum (Figure 3) in which the absorbances of vinyl protons are absent and those of methylene and methine protons are present. SEC results show that PAMP polymers generally have broader MWD than the PDMA polymers (Table 2), indicating the occurrence of deactivation of the growing polymer chain. The cause of the MWD broadening may have been due to residual *N*-methylpiperazine that was difficult to remove completely from the monomer during the monomer preparation. The resulting protonation of the polymeric anions broadens the MWD. When initiated in THF by an initiator with Li^+ as counterion or a Li^+/TMEDA complex (Table 2, run 1), the polymerization was heterogeneous and this also tended to broaden the molecular weight distribution of the poly-

Table 1. Anionic Polymerizations of DMA in THF[a]

run no.	initiator	temp (°C)	M_n(calc)[b] ($\times 10^{-3}$)	M_v[c] ($\times 10^{-3}$)	M_n (NMR)[d] ($\times 10^{-3}$)	M_n (SEC)[e] ($\times 10^{-3}$)	MWD
1	TPM-Li[f]	−78	12.4			g	
2	TPM-Cs	0	16.0			9.5	1.86
3	TPM-Cs	−78	2.0	3.1	2.3	2.0	1.08
4	TPM-Cs	−78	3.5	5.1	3.8	3.3	1.06
5	TPM-Cs	−78	16.0	17.8	20.5	15.4	1.07
6	TPM-Cs	−78	24.0	25.8	31.0	22.7	1.07
7	TPM-Cs	−78	48.1			46.5	1.08
8	TPB-K_2	−78	41.6			32.8	1.31
9	TPB-K_2	−78	83.2			81.0	1.24
10	TPB-Cs_2	−78	19.2			16.6	1.76
11	TPB-Cs_2	−78	87.5			82.0	1.08
12	TPB-Cs_2	−78	160.3			135.0	1.52
13	NapCs	−78	27.3			26.0	1.06
14	NapCs	−78	54.6			52.9	1.07
15	NapCs	−78	109.2			100.8	1.08
16	NapCs	−78	218.4			198.6	1.20
17[h]	TPM-Cs	−78	8.8			8.5	1.08
			26.5			25.5	1.09
18[h]	NapCs	−78	8.0			7.9	1.07
			29.1			28.3	1.07

[a] Polymerizations were essentially quantitative (>95%). [b] Calculated from the ratio of monomer to initiator. [c] Calculated from [η] using the reported Mark−Houwink constants of $K = 17.5 \times 10^{-5}$ dL/g and $\alpha = 0.68$ in MeOH.[30] [d] Determined by ^{1}H NMR integration. [e] Calibrated with polystyrene standards. [f] TMEDA was added as complexing agent. [g] Polymer is insoluble in THF. [h] Two-stage polymerization.

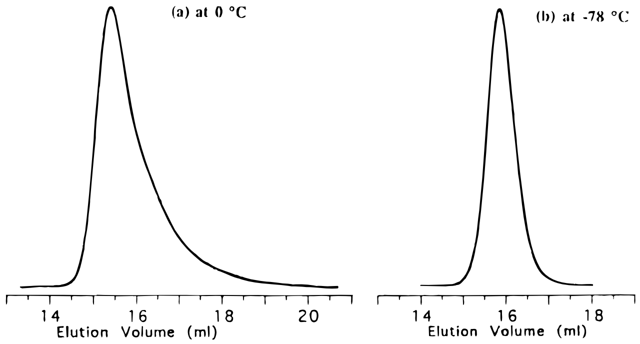


Figure 2. SEC chromatograms of PDMA initiated by TPM-Cs in THF. (a) At 0 °C, run 2 in Table 1: $M_n = 9500$; MWD = 1.86. (b) At −78 °C, run 5 in Table 1: $M_n = 15\,400$; MWD = 1.07.

Table 2. Anionic Polymerizations of AMP in THF[a]

run no.	initiator	temp (°C)	M_n(calc)[b] ($\times 10^{-3}$)	M_n(SEC)[c] ($\times 10^{-3}$)	MWD
1	TPM-Li[d]	−78	15.4	13.8	2.03
2	TPM-Cs	−15	15.8	13.0	2.10
3	TPM-Cs	−78	7.9	6.9	1.26
4	TPM-Cs	−78	15.8	10.7	1.52
5	TPB-Cs_2	−15	50.7	53.0	2.69
6	TPB-Cs_2	−78	23.8	22.7	1.52
7	TPB-Cs_2	−78	47.6	45.2	1.55

[a] Polymerizations were essentially quantitative (>95%). [b] Calculated from the ratio of monomer to initiator. [c] Calibrated with polystyrene standards. [d] TMEDA was added as complexing agent.

mer. At higher reaction temperatures (−15 °C), the polymerization of AMP produced PAMP with broader molecular weight distributions (Table 2, runs 2 and 3).

The above indicates the absence of transfer and termination reactions in the polymerization of DMA and AMP at −78 °C. The broader molecular weight distribution and lower molecular weights observed at higher temperatures apparently are due to factors other than adventitious impurities. Possible deactivation reactions could be (a) deprotonation of the methine proton in the PDMA forming a stabilized carbanion (Scheme 2), (b) deprotonation of the methyl or methylene groups α to the amide nitrogen forming a dipole-stabilized anion[22]

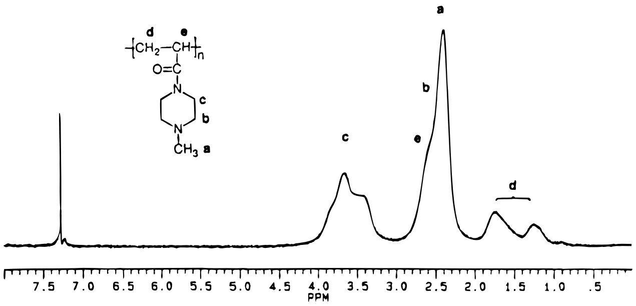
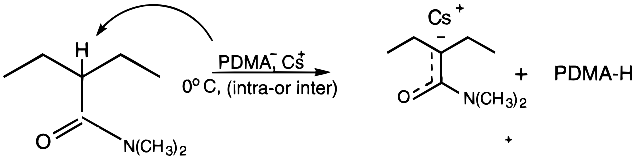
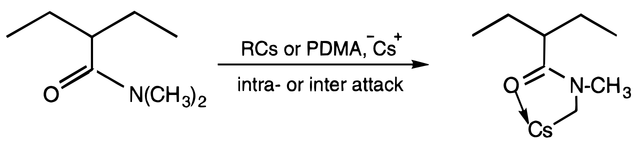


Figure 3. ^{1}H NMR spectrum (360 MHz) of PAMP (Table 2, run 6) in $CDCl_3$ at 30 °C.

Scheme 2

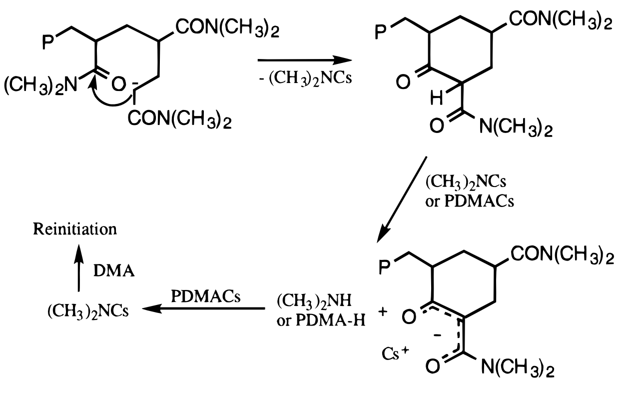


Scheme 3

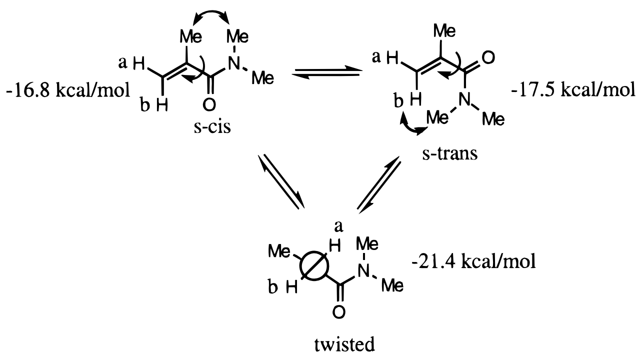


(Scheme 3), or (c) intra- or intermolecular attack of the propagating anion on the amide carbonyl group analogous to the demonstrated termination reaction involving PMMA anion[23] (Scheme 4). We believe that inter- or, perhaps more likely, intramolecular attack of carbanion on the penultimate amide group is most probable. Only this mechanism appears to account well for both the low molecular weight tailing and for the lower M_n values observed. Thus an acidic β-ketoamide is formed with generation of a highly basic dimethylamide anion that could be a reasonably effective initiator for DMA. More likely, however, the dimethylamide anion or PDMACs reacts with the β-ketoamide to give the highly stable enolate that may be incapable of initiation of DMA or would initiate slowly. The dimethylamine generated may react further with PDMACs to produce $(CH_3)_2NCs$

Scheme 4



Scheme 5



that could initiate DMA. Thus, the reaction sequence of Scheme 4 could lead to the termination of two chains. The reinitiation of DMA by $(CH_3)_2NCs$ could then lead to the formation of additional low molecular weight PDMA.

The mechanisms shown in Schemes 2 and 3 do not account well for the experimental results. At least for intramolecular proton transfer the propagating chains are merely isomerized and continue to be capable of further propagation since the anions formed seem at least as basic as the enolate precursors.

Attempted Anionic Polymerization of MAMP and DMMA. On addition of *N*-methacryloyl-*N*′-methylpiperazine (MAMP) to the TPM-Cs carbanion solution in THF at −78 °C, a slow color change (5 min) from red to colorless occurred, consistent with monomer initiation. After 3.5 h at −78 °C, the reaction was quenched by the addition of a small amount of methanol. No polymer was recovered by precipitation in hexane. The ^1H NMR spectrum of reaction mixture obtained upon the evaporation of THF was found to be identical to that of the monomer. The polymerization of this monomer was also unsuccessful at higher reaction temperature (−15 °C) or longer reaction time (100 h). The absence of polymerization of *N*,*N*-dimethylmethacrylamide (DMMA) was also noted in THF in the presence of TPM-Cs at −78 °C. Interestingly, DMMA and MAMP are readily polymerized by radical initiators at 50 °C.

The lack of polymerizability of DMMA and MAMP in these anionic polymerizations may be due to insufficient stabilization of the amide enolate intermediate as a result of nonbonded interactions occurring between the α-methyl group or the vinyl proton and the *N*-methyl groups as illustrated in Scheme 5. Such interactions are expected to cause twisting of the carbonyl−vinyl single bond, leading to less effective overlap of the vinyl and carbonyl π bonds usually found in the planar conformation. MNDO calculations indicate an energy minimum for a twisted monomer conformation having a dihedral angle of ~85.6° between the C=O and $C{=}CH_2$ bonds. The energy of this conformation (−21.4 kcal/mol) lies ~4.0 kcal/mol below that of the s-cis (−16.8 kcal/mol) or the s-trans (−17.5 kcal/mol) conformation, neither of which represents a local minimum. Kodaira and co-workers[24] also concluded that DMMA existed in a twist conformation on the basis of ^1H and ^{13}C NMR data. The reduced π overlap between vinyl and carbonyl groups should result in much less stable enolate anions upon monomer addition, thus greatly decreasing polymerization rates and plausibly enhancing side reactions.

Stereochemistry of PDMA and PAMP polymers. Highly isotactic polymers of DMA were first prepared by Butler et al.[14a] in 1960, using an anionic polymerization in toluene initiated with ethyllithium. These polymers were easy to crystallize so that no annealing treatment was necessary to develop crystallinity. The atactic and isotactic polymers prepared by free radical and anionic initiators, respectively, show large differences in wide-angle X-ray patterns. The most striking differences between atactic and isotactic PDMA could be seen in their melting points and solubilities. The isotactic polymer melts at least 200 °C higher than the atactic stereoisomer. Benzene is a solvent for atactic PDMA but a nonsolvent for isotactic PDMA. Isotactic PDMAs have higher hydrolysis rates under acidic conditions similar to that reported in ref 14a than atactic polymers.[14a] In addition, the analogous poly(*N*,*N*-dibutylacrylamide), synthesized under conditions similar to that reported in ref 14a, has been reported by Badami[25] to be highly isotactic, existing in the solid state as a 3_1 helix.

The first NMR study on the tacticity of PDMA was reported by McGrath et al.,[15a−c] who found large tacticity differences between PDMA polymers obtained by radical polymerization initiated with azobisisobutyronitrile (AIBN) in benzene and those obtained by anionic polymerization in benzene, THF, or hexane at 25 °C initiated by *sec*-butyllithium. The authors suggested that the polymers prepared by radical polymerization mostly are syndiotactic, while the polymers prepared by anionic polymerization are mostly isotactic. Our current results indicate significant differences in the ^{13}C NMR between the polymers prepared in THF at −78 °C in the presence of Li^+ and Cs^+ counterions. The carbonyl ^{13}C NMR spectra (Figure 4) show tacticity differences in the carbonyl region. Three distinct peaks were observed in the downfield region at 174.2−174.6 ppm. According to McGrath and co-workers[15] and in accord with the X-ray studies of Butler et al.,[14] the peak at 174.2 ppm is assigned to the isotactic triads. The absolute triad assignments for the other two peaks are not yet clear.[15c] According to the above assignments, the ^{13}C NMR spectrum in Figure 4 shows isotactic content decreasing with increasing counterion size. In the case of the polymer prepared in the presence of Li^+, a strong absorption at 174.2 ppm and a smaller peak at 174.6 ppm were observed, indicating a relatively large (~54%) isotactic content and a lower syndio- or heterotactic content in this polymer. For the sample, prepared by radical polymerization ($M_w/M_n = 3.90$), very low (<3%) isotactic content was obtained. On the other hand, the methyl carbons show two distinct peaks at 37.2 and 35.8 ppm. Methine carbon absorbs at 36.2 ppm. The peaks between 33.8 and 35.3 ppm were assigned to methylene carbons. In the case of the

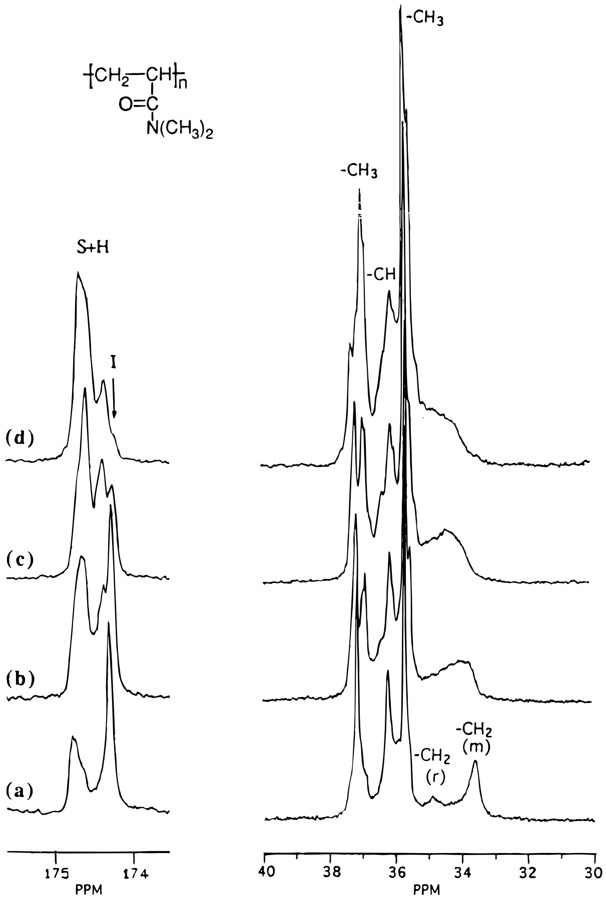


Figure 4. ^{13}C NMR spectra of PDMA in $CDCl_3$ at 30 °C, initiated by (a) TPB-Li_2, (b) TPB-K_2, (c) TPB-Cs_2, or (d) $(NH_4)_2S_2O_8 + Na_2S_2O_5$.

polymer prepared in the presence of Li^+, two distinct peaks were observed at 34.9 and 33.8 ppm. According to McGrath and co-workers,[15] the peaks were assigned to racemic (~27%) and meso (~73%) dyad sequences, respectively. With an increase in couterion sizes, the meso peak becomes smaller, while the racemic peak becomes larger. This is consistent with the carbonyl ^{13}C NMR results, since the radical polymer has very low meso content. This is also supported by the solubility differences between two polymers. The high isotactic content in some of the PDMA samples might be responsible for their insolubility in THF. Furthermore, these differences in stereoregularity are also expressed in the glass transition temperatures (T_g) obtained by DSC. The T_g's of the polymers prepared by TPB-Cs_2 (Table 1, run 5) and TPB-Li_2 (Table 1, run 1) had T_g values of 126 and 121 °C, respectively. The polymer prepared in the presence of TPB-K_2 (Table 1, run 8) had an intermediate T_g value of 124 °C. Decreases in T_g with increasing isotactic content are in agreement with results reported by Mohajer et al.,[15d] who reported that the T_g of PDMA changed from 120 to 112 °C when the isotactic content increased from 14 to 41%. A decrease in T_g with increasing isotactic content has also been observed for poly(methyl methacrylate).[26]

The stereoregularity differences of the PAMP polymers initiated by TPM-Li and by TPM-Cs are illustrated in Figure 5, which shows the corresponding ^1H NMR spectra. The relatively sharp peak of CH_2(c) may indicate a relatively high stereoregularity of PAMP initiated by TPM-Li. The spectra for the polymers initiated by TPM-Cs or TPM-Li + TMEDA show two quite broad peaks of CH_2(c) indicating lower stereoregularity.

The solubilities of these polymers correlate with the above differences in stereoregularity. The solubilities of PDMA and PAMP are reported in Table 3. Solvents such as water, methanol, and chloroform are good solvents for PDMA with the exception of PDMA prepared in the presence of Li ion, where water solubility is partial. The presence of the *N*-alkyl groups results in greater solubility in organic solvents than polyacrylamide, which is insoluble in practically all organic solvents. The PDMA polymers obtained by radical or anionic polymerization in the presence of Cs^+ counterion

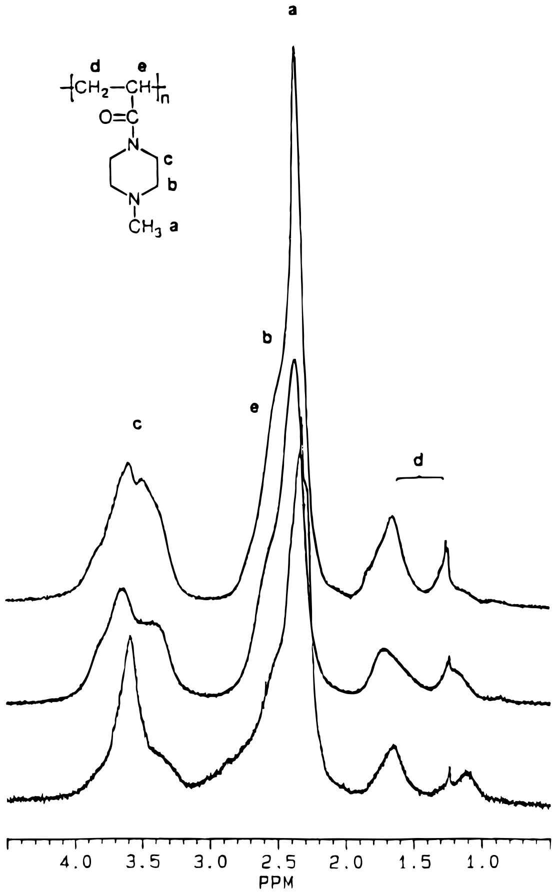


Figure 5. ^1H NMR spectra of PAMP in $CDCl_3$: (bottom) initiated by TPM-Li; (middle) initiated by TPM-Cs; (top) initiated by TPM-Li + TMEDA.

Table 3. Solubilities of PDMA and PAMP Polymers[c]

samples	initiator	MeOH	H_2O	$CHCl_3$	CH_2Cl_2	THF	TOL	DMF	DOX
PDMA	radical[b]	S	S	S	S	S	S	S	S
PDMA	RLi	S	P	P	P	I	I	I	I
PDMA	TPM-Li	S	P	P	P	I	I	I	I
PDMA	TPM-Li[c]	S	S	S	S	P	I	P	I
PDMA	TPB-K_2	S	S	S	S	P	I	S	P
PDMA	TPB-Cs_2	S	S	S	S	S	P	S	S
PDMA	TPM-Cs	S	S	S	S	S	P	S	S
PAMP	radical[b]	S	S	S	S	S	S	S	S
PAMP	RLi	S	S	S	S	I	I	I	I
PAMP	TPM-Li	S	S	S	S	I	I	I	I
PAMP	TPM-Li[c]	S	S	S	S	S	I	S	P
PAMP	TPB-Cs_2	S	S	S	S	S	P	S	S

[a] S, soluble; P, partially soluble; I, insoluble; R, *n*-butyl, *sec*-butyl, *tert*-butyl; TPB-Li_2, TPB-K_2, and TPB-Cs_2, (1,1,4,4-tetraphenylbutyl)dilithium, -dipotassium, and -dicesium, respectively; TPM-Li, (triphenylmethyl)lithium; TPM-Cs, (triphenylmethyl)cesium; DMF, dimethylformamide; TOL, toluene; DOX, dioxane. [b] $(NH_4)_2S_2O_8 + Na_2S_2O_5$. [c] TMEDA was added as a complexing agent.

are soluble in THF and even in nonpolar solvents such as toluene, while those prepared by anionic polymerization initiated by *n*-BuLi, *s*-BuLi, *t*-BuLi, and (triphenylmethyl)lithium in THF are insoluble in THF, as also reported by McGrath[15a] in the case of *sec*-butyllithium. As pointed out above, these differences in solubility appear to correlate with the stereochemistry, which is quite different for various systems.[14,15a,27−29] An increase in cation size or coordination leads to an increase in solubility of the DMA polymers in THF. Thus, initiation of DMA with a TPB-K_2 initiator results in polymers that are more soluble than those initiated by the initiators with Li^+ counterions but less soluble than PDMA polymerized by Cs initiators. Addition of TMEDA as a complexing agent for Li^+ counterion also improves the solubility in THF, apparently as a result of the formation of a Li^+−TMEDA complex, which in turn decreases the stereoregularity of the chain.

In conclusion, we have demonstrated the anionic polymerization of two hydrophilic polar monomers, DMA and AMP, in THF at −78 °C using various nucleophilic initiators. Delocalized carbanions such as diphenylmethyl or triphenylmethyl or electron transfer initiators such as naphthalene radical anion can be employed, but initiators with Cs^+ as counterion are preferred, allowing the polymerizations to proceed in homogeneous media. Good correlation was observed between the calculated M_n and the experimental M_n determined by SEC and ^1H NMR. The resulting polymers show narrow molecular weight distributions, suggesting that the polymerizations proceed without significant chain transfer and termination. The rates of initiation and propagation were found to be extremely rapid, allowing quantitative conversions within 5 min at −78 °C. The effect of temperature on the polymerization was also observed. Side reactions apparently occurred at −15 °C or higher. Polymerization stereochemistry was found to be dependent on counterion. Thus, with Li^+, the isotactic content is greater than with K^+ and Cs^+ as counterions. The tacticity differences are also expressed by differences in glass transition temperatures and by solubility differences in solvents such as THF.

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