Group Transfer Polymerization of *N*-Substituted Maleimides

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ABSTRACT: Group transfer polymerization (GTP) of *N*-phenylmaleimide (NPM), *N*-phenylcitraconimide (NPC), and *N*-(4-dimethylaminophenyl)maleimide (NAPM) was investigated with methyl trimethylsilyl dimethylketene acetal (MTDA) as initiator and tetrabutylammonium bibenzoate (TBAB) as catalyst. NPM can be polymerized by GTP initiators and can be incorporated into statistical copolymers with methyl methacrylate (MMA). These reactions do not exhibit the characteristics of living polymerization. NPM is more reactive than MMA in GTP-initiated copolymerizations, and at low concentration effectively inhibits the polymerization of MMA. Poly(MMA-*block*-NPM) can be obtained by adding NPM to living poly(MMA), but the block copolymer is polydisperse in size and composition. NAPM can also be polymerized, but NPC gave no polymers *via* GTP. Poly(NPM) and poly(MMA-*co*-NPM) prepared by GTP show excellent thermal stability.

KEY WORDS Group Transfer Polymerization / *N*-Phenylmaleimide / *N*-Phenylcitraconimide / *N*-(4-Dimethylaminophenyl)maleimide / Methyl Trimethylsilyl Dimethylketene Acetal / Tetrabutylammonium Bibenzoate / Methyl Methacrylate / Living Polymerization / Thermal Stability /

Group transfer polymerization (GTP) has been shown to be a very useful method for the preparation of methacrylate polymers with precisely controlled molecular weights, molecular weight distributions, and macromolecular architectures.[1,2] Sogah and coworkers have reported that GTP is also useful for polymerization of acrylates, *N,N*-dimethylacrylamide, acrylonitrile, methacrylonitrile, and α-methylene-γ-butyrolactone.[3]

Vinyl monomers possessing one carbonyl group such as (meth)acrylates can be polymerized with appropriate GTP initiators and the mechanism of polymerization of such monomers has been studied intensively and systematically.[4-6] However, GTP of vinylene monomers featuring 1,2-dicarbonyl substituted structures has not been described.

N-Substituted maleimides are vinylene monomers useful in the preparation of heat resistant variants of common vinyl polymers. The radical and anionic polymerization behavior of such monomers and the thermal properties of the resulting polymers have been extensively studied by many workers.[7-12] We report in this paper a preliminary investigation of the GTP behavior of *N*-substituted maleimides, with the objective of preparing architecturally well-defined polymers with improved thermal properties.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was distilled from lithium aluminum hydride/benzophenone ketyl immediately prior to use. *N,N*-Dimethylformamide (DMF) was distilled from barium oxide (BaO) under reduced pressure. *N*-Phenylmaleimide (NPM) was commercially available and used after several recrystallizations. Methyl methacrylate (MMA) was purified by vacuum

distillation to remove inhibitors and protonic impurities. The GTP initiator, methyl trimethylsilyl dimethylketene acetal (MTDA), was purchased from Aldrich Chemical Co. and was purified by vacuum distillation.

Preparations

Preparation of N-Substituted Maleimides. N-Phenylcitraconimide and N-(4-dimethylaminophenyl)maleimide were prepared by the reaction of citraconic anhydride or maleic anhydride with the corresponding anilines according to methods described in the literature,[13,14] followed by several recrystallizations.

N-Phenylcitraconimide (NPC): In a 1000 ml three-necked flask provided with a stirrer, a reflux condenser and a dropping funnel were placed 44.8 g (0.40 mol) of citaconic anhydride and 500 ml of ethyl ether at 0°C. Freshly distilled aniline (37.3 g, 0.40 mol) was added dropwise over 30 min to the flask through the dropping funnel. A yellow precipitate was formed immediately upon addition of the aniline. The reaction mixture was stirred overnight. The yellow powder (78 g, 95%) was collected by suction filtration and added to a mixture of 200 ml of acetic anhydride and 20 g of anhydrous sodium acetate. The resulting mixture was heated with stirring until the internal temperature reached 90—95°C. Heating and stirring were maintained for one hour. After cooling, the reaction mixture was poured into a large amount of ice water and free acid was neutralized with sodium carbonate. The product precipitated was collected by suction filtration and washed three times with ice-cold water and once with petroleum ether. Recrystallization from cyclohexane gave light-brown needles. Yield 44.4 g (62%); mp 97—98°C (lit.,[14] mp 98—99°C). *Anal.* Calcd for $C_{11}H_9NO_2$: C, 70.6%; H, 4.9%; N, 7.5%. Found: C, 70.6%; H, 4.9%; N, 7.5%. ^{1}H NMR (200 MHz, CDCl_3): δ 2.20 (s, 3H), 6.45 (s, 1H), 7.40 (m, 5H).

N(4-Dimethylaminophenyl)maleimide

(NAPM): NAPM was prepared in the manner described above. Recrystallization from cyclohexane gave red-brown needles. Yield 62%; mp 156—157°C (lit.,[15] mp 153—154°C). *Anal.* Calcd for $C_{12}H_{12}N_2O_2$: C, 66.7%; H, 5.6%; N, 13.0%. Found: C, 66.4%; H, 5.7%; N, 12.8%. ^{1}H NMR (200 MHz, CDCl_3): δ: 2.95 (s, 6H), 6.75 (m, 4H), 7.10 (d, 2H).

Preparation of Tetrabutylammonium Bibenzoate. The GTP catalyst, tetrabutylammonium bibenzoate (TBAB), was prepared from benzoic acid and aqueous tetrabutylammonium hydroxide (TBAOH) as per ref 6. To a separatory funnel was added 10.0 g (0.082 mol) of benzoic acid and 80 ml of 40% aqueous TBAOH. The mixture was shaken until homogeneous then extracted with 3×50 ml of CH_2Cl_2. To the combined extracts was added 10.0 g of benzoic acid, and the solution was dried over $MgSO_4$, filtered and stripped. The residual solid was dissolved in 250 ml of warm THF and the volume was reduced to 125 ml under aspirator pressure. To the partly crystallizing mixture was added 250 ml ether (in parts) and the mixture allowed to stand overnight. The product was filtered, washed with ether and dried under high vacuum; mp 102—104°C (lit.,[6] mp 103—105°C). *Anal.* Calcd for $C_{30}H_{47}NO_4$: C, 74.2%; H, 9.8%; N, 2.9%. Found: C, 73.4%; H, 9.9%; N, 2.9%. ^{1}H NMR (200 MHz, CDCl_3): δ 0.86 (t, 12H), 1.28 (m, 8H), 1.47 (m, 8H), 3.13 (t, 8H), 7.33 (m, 6H), 8.06 (m, 4H).

Polymerization Procedures

Polymerizations were performed in glass reaction flasks under purified nitrogen atmosphere using syringe techniques for introduction of liquid reactants and solvents. Stirring was effected by a magnetic stirrer. All glassware was dried prior to assembly by storing overnight in a 150°C oven.

GTP of N-Substituted Maleimides. To a dry three-necked 300 ml round bottomed flask equipped with a magnetic stir bar and sealed

with a rubber septum was charged 50 ml of THF *via* syringe. The desired amount of GTP initiator was then added *via* syringe followed by 11.0 mol% (relative to initiator) of the GTP catalyst in THF solution. After these were allowed to stir for approximately 5 min, a solution of the *N*-substituted maleimide in 50 ml of THF was added *via* syringe at a rate of 5 ml per minute so as to keep the exotherm of reaction to a minimum. After an hour polymerization was terminated with a solution of 4 drops of hydrochloric acid in 5 ml of methanol and the reaction mixture was poured into an ether–methanol (volume ratio 3:1) mixture. The precipitate was collected by filtration, washed with ether and methanol, and dried *in vacuo*. *Anal*. Calcd for $(C_{10}H_7NO_2)_n$: C, 69.4%, H, 4.1%; N, 8.1%. Found: C, 67.6%; H, 4.1%; N, 7.8%.

Statistical Copolymerization of MMA and NPM. Statistical copolymerizations were carried out by feeding a mixture of monomers into the mixture of initiator and catalyst in the manner described above.

Preparation of Poly(MMA-block-NPM). To a 300 ml round bottomed flask fitted with a rubber septum was added 50 ml of THF, 0.339 ml (1.67 mmol) of the GTP initiator and 1.0 mol% (relative to initiator) of the GTP catalyst in THF solution. MMA (5.35 ml, 50.0 mmol) was added *via* syringe at a rate of 1.0 ml per minute to give a theoretical $\bar{M}_n$ of 3000. An hour after an exothermic reaction occurred, a 11.3 ml (10.0 mmol of MMA) sample of the polymer solution was withdrawn. An additional 4.28 ml (40.0 mmol) of MMA was added to give a theoretical $\bar{M}_n$ of 6000, followed by the addition of more GTP catalyst (0.65 ml, 0.0206 M in THF). An hour after the addition of the GTP catalyst, a second 6.27 ml (10.0 mmol of MMA) sample of the polymer solution was withdrawn. A solution of 5.20 g (30.0 mmol) of NPM in 20 ml of THF was added at a rate of 2.0 ml per minute, followed by the addition of more GTP catalyst (7.30 ml, 0.0206 M in THF). After an hour polymeriza-

tion was terminated by the addition of 4 drops of hydrochloric acid in 5 ml of methanol and then the reaction mixture was poured into 1000 ml of a hexane–ether–methanol (volume ratio 5:3:2) mixture. The precipitate was collected by filtration, washed with hexane, ether, and methanol, and dried *in vacuo*.

Measurements

^{1}H NMR spectra were recorded at 200 MHz on a Bruker/IBM 200AC spectrometer. ^{13}C NMR spectra were recorded at 75.4 MHz on a Varian XL-300 spectrometer. Infrared (IR) spectra (KBr disk) were recorded on a JEOL JIR-100 FT-IR spectrometer. Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Elmental analyses were performed by the University of Massachusetts Microanalytical Laboratory. Gel permeation chromatography (GPC) was measured on a Waters GPC-501 instrument equipped with two Ultrastyragel™ Linear and one Ultrastyragel™ 10^3 Å column and a differential refractometer detector, using THF as eluent (flow rate 1.0 ml min^{-1}). Molecular weights were calibarated with a set of monodisperse polystyrene standards. Thermogravimetric analyses were carried out on a Perkin-Elmer TGS-2 Thermogravimetric Analyzer in a nitrogen stream at a heating rate 10°C per minute.

RESULTS AND DISCUSSION

GTP of N-Substituted Maleimides

The polymerization of *N*-substituted maleimides using GTP procedures might be expected to proceed as illustrated in Scheme 1.[16]

The NPM homopolymers obtained by this method were yellow powders which were soluble in THF, dimethyl sulfoxide (DMSO), DMF, and dichloromethane, and insoluble in chloroform, ether, alcohol, and hydrocarbon solvents.

Figure 1 shows a typical ^{1}H NMR spectrum

of poly(NPM) prepared by GTP. The signals observed from 6 to 8 ppm are assigned to phenyl protons; the broad peaks from 3 to 5 ppm are assigned to the methine protons in the polymer main chain. The breadth of these

signals is attributed to the stiffness of the main chain and to the different configurations (*cis* or *trans*) of the succinimidyl backbone protons. No additional signals other than those due to the solvent (DMSO and H_2O) are observed. This suggests that addition polymerization of the vinylene group takes place without appreciable side reactions such as ring-opening of the imide group.[11]

Figure 2 shows a typical ^{13}C NMR spectrum of poly(NPM) prepared by GTP. The signals assigned to the carbonyl and phenyl carbons of poly(NPM) are observed at 176 ppm and from 125 to 132 ppm, respectively. The broadened signal from 38 to 48 ppm is assigned

Scheme 1.
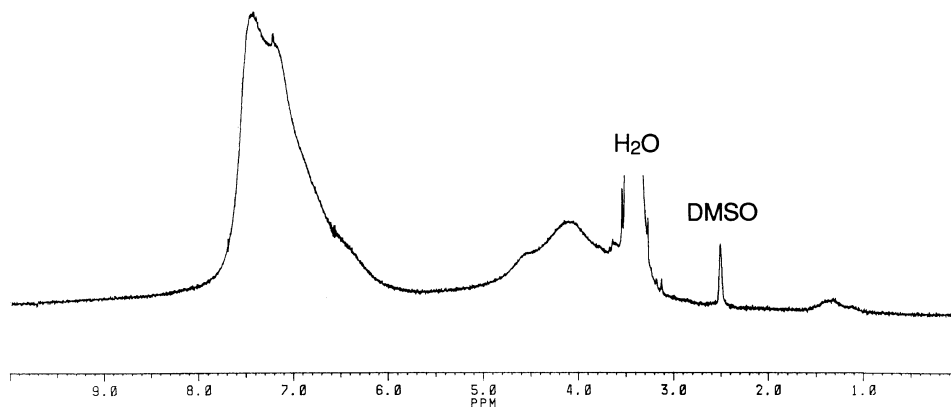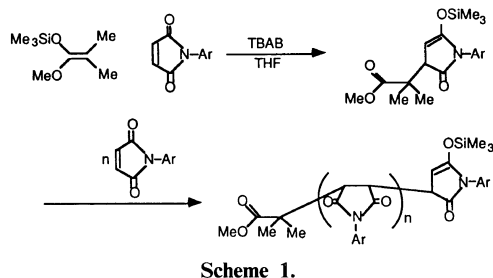
Figure 1. ^1H NMR spectrum of poly(NPM) (run 3 in Table I).
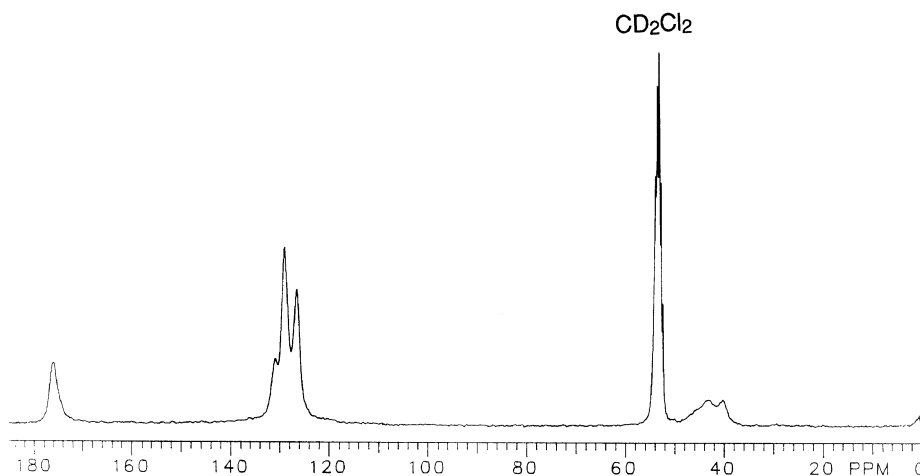
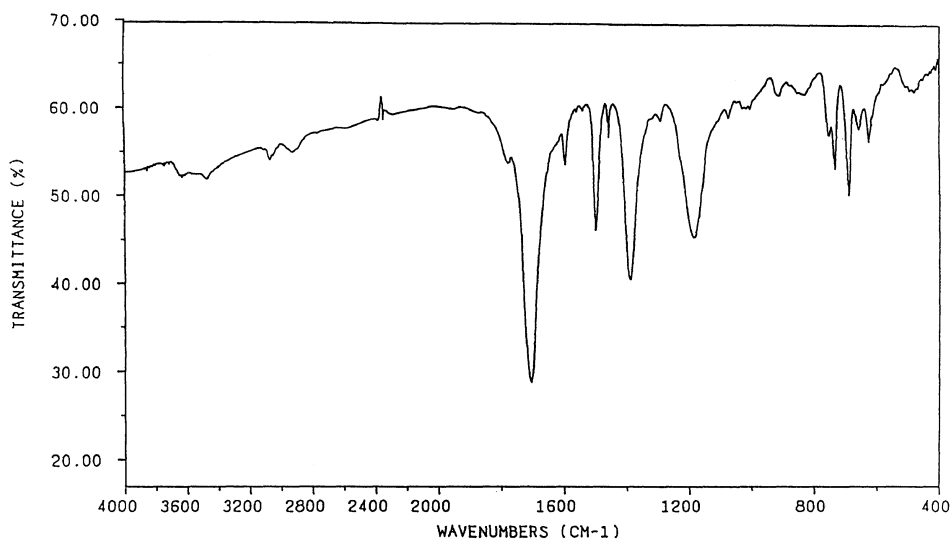**Figure 2.** ^{13}C NMR spectrum of poly(NPM) (run 3 in Table I).

Figure 3. IR spectrum of poly(NPM) (run 3 in Table I).

to the methine carbons in the polymer main chain. The broadening of the methine carbons reflects the complex microstructure of the main chain.

Figure 3 shows a typical IR spectrum of poly(NPM) prepared by GTP. The absorption bands due to the imide ring are observed at 1778 (C=O), 1705 (C=O), and 1390 (cm^{-1} C–N–C). The absorption bands assigned to the aromatic ring are observed at 3066 (CH), 1597 (C=C), 1500 (C=C) and 754 and 690 cm^{-1} (monosubstitution). The strong ethylenic CH stretch at 840 cm^{-1}, which is characteristic of NPM monomer, is absent, indicating that monomer and polymer have been effectively separated.[18]

Figure 4 shows a typical GPC trace of poly(NPM) prepared by GTP. Narrow molecular weight distributions have not been achieved.

Table I summarizes the results of GTP of NPM initiated with MTDA. The polymers have low intrinsic viscosities (0.08—0.15 dl g^{-1}) under all of the conditions investigated. There are no significant differences among the intrinsic viscosities (*ca.* 0.1 dl g^{-1}) of poly-(NPM)s obtained under these reaction condi-
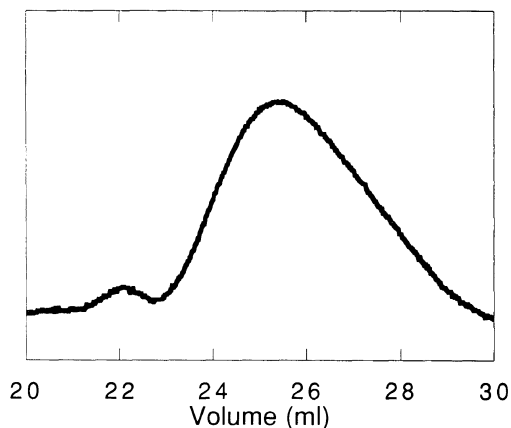

Figure 4. GPC trace of poly(NPM) (run 3 in Table I).

tions (polymerization in THF at room temperature by slow monomer addition), in spite of the changes in monomer/initiator mole ratio. These results indicate that chain transfer or termination reactions occur during GTP of NPM, and that living polymerization conditions have not been realized. The highest molecular weight polymer ([η] = 0.15 dl g^{-1}) was obtained with DMF as solvent, though the yield was low. Decreasing the polymerization temperature to $-78°$C caused a reduction in yield without improvement in molecular weight

Table I. GTP of N-phenylmaleimide

Run no.	Monomer $\mathrm{mol\,l^{-1}}$	Initiator $\mathrm{mol\,l^{-1}}$	Conditions	Yield wt%	$[\eta]^a$ $\mathrm{dl\,g^{-1}}$	M_n $\times 10^{-3}$	M_w/M_n
1	0.30	0.06	b	100.0	0.11	11.2	5.1
2	1.0	0.20	b	98.3	0.10	15.2	3.1
3	3.3	0.015	b	48.4	0.10	10.9	3.7
4	1.0	0.05	b	53.1	0.10	20.1	2.4
5	1.0	0.05	c	33.7	0.15	f	f
6	1.0	0.05	d	36.1	0.08	11.3	2.7
7	1.0	0.05	e	69.3	0.05	7.6	3.1
8	0.30	0.006	b	21.9	0.08	9.2	2.5
9	1.0	0.02	b	27.1	0.10	16.1	2.2

[a] 30°C DMF; b, THF, room temperature, slow monomer addition; c, DMF as solvent; d, THF, $-78°C$; e, THF, rapid monomer addition; f, Insoluble in THF.

Table II. Compolymerization of MMA and NPM

Run no.	[MMA] $\mathrm{mol\,l^{-1}}$	[NPM] $\mathrm{mol\,l^{-1}}$	$\dfrac{[\mathrm{MMA}]+[\mathrm{NPM}]}{[\mathrm{Initiator}]}$	Yield wt%	NPM content[a] mol%
10	0.99	0.02	10	3.2	50
11	0.95	0.05	10	8.3	66
12	0.85	0.15	10	22.9	85
13	0.30	0.10	10	34.3	87
14	0.30	0.30	10	63.8	91
15	0.30	0.30	50	1.0	92
16	0.25	0.75	10	81.3	96

[a] Calculated from elemental analysis.

or polydispersity (run 6). Rapid monomer addition (run 7) caused a significant reaction exotherm, with the temperature rising rapidly from 25 to 43°C. This procedure gave a high yield, but a low molecular weight polymer.

Attempts at GTP of NPC failed. The color of the reaction mixture changed from light brown to purple when NPC was charged ([M] = 0.20 mol l^{-1}, [I] = 0.04 mol l), but no polymers were obtained. This result may be explained by steric hindrance of the 1,1,2-trisubstituted double bond of NPC, and is in agreement with the results of Marvel and coworkers on base-catalysed polymerization of citraconimide.[17]

The electron donating dimethylamino group of NAPM was expcted to reduce the acidity of the imide protons, and thereby to reduce interference from proton transfer reactions that compete with the propagation step. In fact, NAPM can be polymerized by GTP in THF solution heterogeneously ([M] = 0.12 mol l^{-1}, [I] = 0.024 mol l^{-1}, room temperature, slow monomer addition). The yield was 96% of a reddish yellow powder which was soluble in chloroform, DMSO and DMF, and insoluble in THF, ether, alcohol, and hydrocarbon solvents. The intrinsic viscosity ($[\eta]_{\mathrm{DMF}}^{30°C} = 0.06$ dl g^{-1}) was not improved in comparison with the polymerization of NPM.

Statistical Copolymerization of MMA and NPM

Statistical copolymers of NPM and MMA

could be prepared by GTP; the results are listed in Table II. These copolymers consist of about 90 mol% NPM over a wide range of monomer feed compositions (Figure 5). NPM is apparently incorporated much more rapidly into the copolymer than is MMA, though reactivity ratios have not been determined. These results are consistent with the expected increased Michael acceptor activity of NPM as compared to MMA. In fact, NPM at low concentrations (e.g., runs 10 and 11) behaves effectively as an inhibitor of MMA polymerization, indicating that cross-propagation from the NPM chain end to MMA monomer is inefficient.
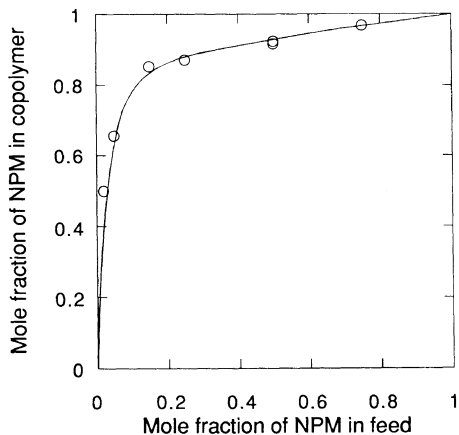

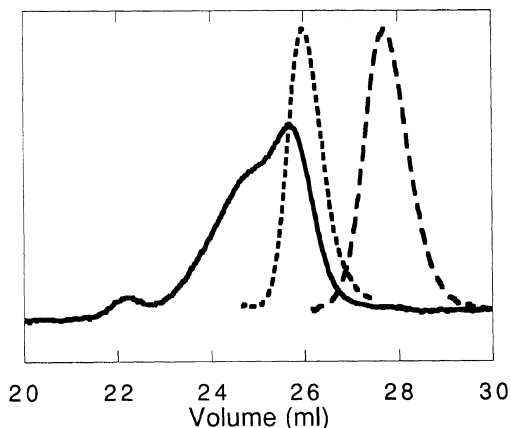**Figure 5.** MMA–NPM copolymer composition curve.

Figure 6. GPC traces of poly(MMA-*block*-NPM) and the trace obtained upon sequential additions of MMA.
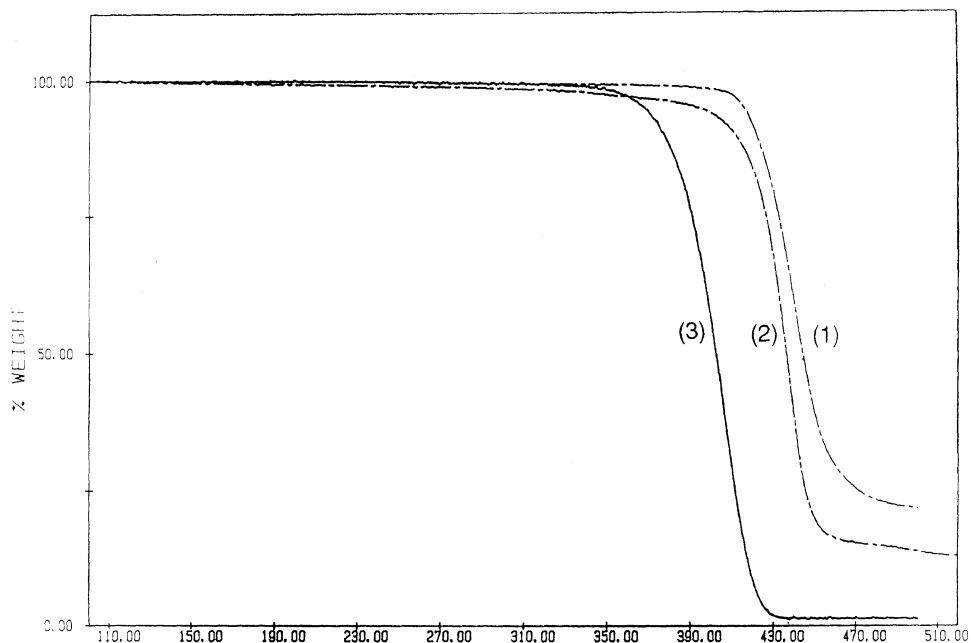

Figure 7. Thermogravimetric analysis: (1) poly(NPM) (run 3 in Table I); (2) poly(MMA-*co*-NPM) (run 13 in Table II); (3) poly(MMA).

Preparation of Poly(MMA-block-NPM)

Figure 6 shows the GPC traces of poly-(MMA-*block*-NPM) and those obtained upon sequential additions of MMA. On the basis of elemental analysis, 24 mol% of NPM was incorporated into the block copolymer. The number average molecular weight ($\bar{M}_n$) and the polydispersity ($\bar{M}_w/\bar{M}_n$) were 14100 and 1.9, respectively. These results suggest that poly-(MMA-*block*-NPM) can be obtained by adding NPM to living poly(MMA), but the block copolymer is polydisperse in size and composition. An attempt to add MMA to "living" poly(NPM) failed to produce any evidence of chain extension.

Thermal Stability of the Polymers

Poly(NPM) and poly(MMA-*co*-NPM) showed good thermal stability. As shown in thermogravimetric analysis (Figure 7), poly-(NPM) undergoes no substantial weight loss below 400°C. The half weight loss temperature (T_{50}) is about 440°C and the residual weight at 500°C is about 20 wt%. Poly(MMA-*co*-NPM) also shows good thermal stability in comparison with poly(MMA).

CONCLUSIONS

1. NPM can be polymerized by GTP initiators and can be incorporated into statistical copolymers with MMA *via* GTP procedures. These reactions do not exhibit the charcteristics of living polymerizations. NPM is more reactive than MMA in copolymerizations, and at low concentrations effectively inhibits the polymerization of MMA.

2. Poly(MMA-*block*-NPM) can be obtained by adding NPM to living poly(MMA), but the block copolymer is polydisperse in size and composition.

3. NAPM can also be polymerized, but NPC gave no polymers *via* GTP procedures.

4. Poly(NPM) and poly(MMA-*co*-NPM) prepared by GTP show excellent thermal stability.

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