Effect of ortho-Substituents on the Free-Radical Polymerization of N-Phenylmethacrylamides and on the Thermal Stability of the Polymers

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ABSTRACT

Ceiling temperatures (T_c) and reactivities of N-phenylmethacryl-amide (PMAm) and o-substituted PMAm's in free-radical polym-erization and the thermal stability of the polymers obtained were investigated. Although PMAm and o-substituted analogs gave the same T_c, 123°C at 0.64 mol/L in N,N-dimethylformamide, that of 2,6-dimethyl-PMAm was found to be as low as 65°C. These findings are interpreted in terms of steric hindrance as a consequence of the bulkiness of the 2- and 6-substituents and of the rigid and planar structure expected for the polymers. In copolymerization with sty-rene, the o-monosubstituted PMAm's were estimated to be more reactive than PMAm by a factor of about 3 except for o-phenyl-PMAm. The enhanced reactivity of the PMAm with a relatively small o-substituent is explained by ground-state strain of the mono-

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mer tending toward a planar structure. 2,6-Dimethyl-PMAm and
o-phenyl-PMAm showed lower and slightly higher reactivities than
PMAm, respectively, probably due to the blocking effect of these
substituents against the approaching polymer radical. Enhance-
ment of thermal degradation owing to the substitution was confirmed
by means of thermogravimetric analyses of the polymers. The poly-
mers from the 2,6-dimethyl-substituted and the o-monosubstituted
PMAm's exhibited similar maximum-degradation-rate tempera-
tures.

INTRODUCTION

The effects of o-substitution on free-radical polymerization of
phenyl methacrylate (PMA), ascribed mainly to steric factors, are
much more prominent than those of the m- and p-substituents [1-4].
In particular, the ceiling temperature (T_c) of the o-substituted PMA
has been linearly correlated with the steric substituent constant, E_s
[5], as follow [6]:

$$T_c = 41.0E_s + 182.6. \tag{1}$$

This equation implies that the free energy change of polymeriza-
tion relating to T_c decreases with increasing bulkiness of the substit-
uent, and the pronounced role of the steric effect in determining T_c is
emphasized. On the basis of molecular models, it has been claimed
that the polymer is destabilized by steric hindrance due to the inter-
action between the o-substituent and the remainder of the polymer [1,
6]. Furthermore, the relatively small effect of o-substitution of
phenyl acrylate pointed out the role of the α-methyl group of the PMA
[6].
Although the relative reactivity of a monomer is due to a complex
interplay of several factors, the steric effect of the o-alkyl substitu-
ent is the dominant factor governing the reactivity of PMA. The re-
activity toward polystyrene radical relative to styrene, R_{rel}, is given
by Eq. (2) [6]:

$$\log R_{rel} = 0.095E_s + 0.665. \tag{2}$$

However, the quite small value of the coefficient of E_s suggests
that subtle changes in resonance and polar effects caused by the o-
substitution are comparable to the steric effect. While most of the
PMA's showed lower reactivities than PMA, differences in reactivity

were too small to correlate quantitatively with the steric effect sepa-
rately from the resonance and polar effects. This seems to be the
reason why Eq. (2) holds only for the o-alkyl-PMA's.

In this article, N-(o-substituted phenyl)methacrylamides, which are
isoelectronic compounds of the PMA's with the same substituents, are
utilized for determination of T_c in N,N-dimethylformamide (DMF), and
the effect on T_c of the o-substitution is compared with that of PMA. Ac-
cording to the results of the polymerization of N-phenylmethacrylamide
(PMAm) [7] and of the PMA's [1-4], T_c of PMAm, which is lower than
that of PMA, may be decreased further by the o-substitution. In addi-
tion to T_c, reactivities of the PMAm's are estimated by copolymeriza-
tion with styrene. Lowering of T_c may be reflected in the maximum-
degradation-rate temperature (MDT) in thermogravimetric analysis
(TGA) as anticipated on the basis of T_c for 2,6-dimethyl-PMA and
MDT of the polymer from it [1]. Determinations of T_c relating to the
stability of the monomer or the polymer, of the reactivity governed by
the activation energy, and of thermal stability of the polymers are ex-
pected to give indications about the effect of o-substitution on radical
polymerization of the PMAm's.

<div align="center">EXPERIMENTAL</div>

Monomers

PMAm, o-methyl-PMAm, o-methoxy-PMAm, o-chloro-PMAm, o-
phenyl-PMAm, and o-methoxycarbonyl-PMAm were prepared by the
interfacial reactions of methacryloyl chloride with the corresponding
substituted anilines [8-10]. Methacryloyl chloride as benzene solution
(30%) was added to an aqueous solution containing equimolar amounts
of aniline or substituted aniline and sodium hydroxide with stirring at
5°C. Acetonitrile was added by small portions during the reaction so
as to dissolve the monomer in the organic layer. The monomers ob-
tained, except for o-methyl-PMAm, were purified by recrystallization
from ethyl acetate. o-Methyl-PMAm was distilled under reduced pres-
sure. 2,6-Dimethyl-PMAm was also prepared by the interfacial reac-
tion and was recrystallized from ethyl acetate: mp 96.0-96.5°C.

Commercially available styrene was distilled under reduced pres-
sure before use.

Polymerization and T_c Determination

Polymerizations were run in sealed tubes with DMF as solvent. In
order to obtain the proper polymerization rate over the wide tempera-

ture range, 2,2'-azodi-2,4-dimethylvaleronitrile, 2,2'-azodiisobutyro-
nitrile, 1,1'-azodicyclohexane-1-carbonitrile, or di-t-butyl peroxide
was employed as initiator.

The overall rate of polymerization (R_p) was obtained from the
weight of polymer formed. In the case of the o-methyl-PMAm, R_p
was calculated from the amount of residual monomer measured
by gas chromatography.

T_c was calculated by using the following equations [3]:

$$\frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \frac{(k_d E_d/R[M] - k_p E_p/R)}{(k_p - k_d/[M])} + \frac{E_t}{2R} \tag{3}$$

and

$$\lim_{T \to T_c} \frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \infty, \tag{4}$$

where k, E, and R denote the rate constant, the activation energy, and
the gas constant, respectively. The subscripts p, t, and d stand for
propagation, termination, and depropagation, respectively. The numeri-
cal value of $k_p'/k_t^{0.5}$ was calculated from R_p, where k_p' is the apparent
propagation rate constant given by

$$k_p' = k_p - k_d/[M].$$

Copolymerization

Copolymerizations of the PMAm's (M_1) with styrene (M_2) were car-
ried out in sealed tubes at 60°C, and the copolymer compositions were
calculated from elemental analyses, except for those of the o-methyl-
PMAm copolymers which were determined by measuring the amount of
unchanged monomer by chromatography. Monomer reactivity ratios
were obtained by using a nonlinear least squares procedure [11].

Thermogravimetric Analyses

Thermogravimetric analyses and differential thermogravimetric
analyses were carried out by means of a Shimadzu TGA-20B thermo-

balance. About 1.5 mg of the polymer sample was heated at 10°C/min in a nitrogen atmosphere.

NMR Spectroscopy

The ^{1}H-NMR spectra of the monomers and of the polymers in deuterochloroform were recorded on a JEOL JNM PS-100 spectrometer, and tetramethylsilane was used as the internal standard.

RESULTS AND DISCUSSION

T_c of o-Substituted PMAm's

T_c is defined as the temperature at which the free energy change of polymerization is equal to zero or the rate of propagation is the same with that of depropagation [12]. Either an increase or a decrease in stability of a monomer or a polymer may lower T_c. As a consequence of the fast termination of the growing polymer radical, the propagation-depropagation equilibrium in radical polymerization cannot be observed directly. Because, as the temperature is raised to near T_c, R_p will be affected by the equilibrium, the temperature dependence of $k_p'/k_t^{0.5}$ over a wide temperature range as given by Eq. (3) will obviously differ from the ordinary Arrhenius equation.

Figure 1 shows some examples of the plots based on Eqs. (3) and (4), and T_c is determined by extrapolation to the temperature where the slope of the curve becomes infinite. The curve was extrapolated after confirmation of no polymer formation at temperatures above T_c. For instance, the curve for 2,6-dimethyl-PMAm was drawn in view of the fact that the 0.64 mol/L DMF solution of this monomer yielded a definite amount of polymer at 60°C or lower temperatures and that no polymer formation was observed at 65°C or above.

The T_c values thus obtained are summarized in Table 1 together with those for the PMA's reported before [6]. The T_c of N-n-butyl-methacrylamide, 122°C at 0.65 mol/L in ethyl benzoate [7], is actually the same as that of PMAm, corresponding to the quite similar T_c of PMA with that of methyl methacrylate [6]. Although the T_c of the PMA's has been correlated with E_s as expressed by Eq. (1), that of the PMAm's except for 2,6-dimethyl-PMAm, is constant irrespective of the size of the substituent. The small effect of o-substitution on T_c
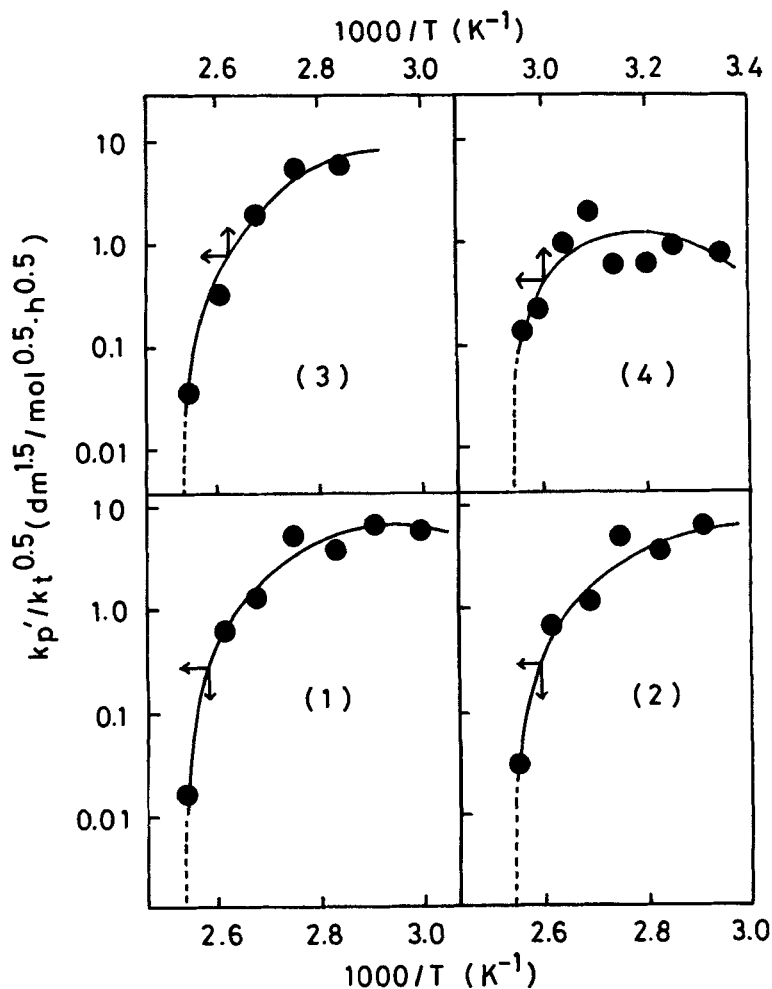
FIG. 1. Determination of T_c for o-substituted PMAm in DMF:
(1) o-chloro-PMAm, (2) o-methoxy-PMAm, (3) PMAm, (4) 2,6-
dimethyl-PMAm.

of PMAm was further confirmed by measuring T_c at different monomer
concentrations in the same solvent.

Figure 2 demonstrates the dependence of T_c on the monomer con-
centration ($[M]_e$) based on the following relation for the polymeriza-
tions of PMAm, o-methoxycarbonyl-PMAm, and 2,6-dimethylPMAm;

TABLE 1. T_c of Substituted PMAm and PMA at 0.64 mol/L

	T_c, °C	
Substituent	PMAm[a]	PMA[b]
None	123	146
o-Methoxy	123	145
o-Chloro	123	139
o-Methyl	123	138
o-Phenyl	123	100
o-Methoxycarbonyl	123	112
2,6-Dimethyl	65	73

[a]This work, in DMF.
[b]Reference 6, in p-xylene.

$$\ln [M]_e = \frac{\Delta H_{ss}}{RT_c} - \frac{\Delta S^0_{ss}}{R},$$

where the subscript ss stands for polymerization of the monomer in solution to the polymer in the same solvent, and ΔH and ΔS^0 are the enthalpy change and the entropy change at a standard state of 1 mol/L monomer concentration, respectively. It is apparent from Fig. 2 that the constant T_c for the un- or the monosubstituted PMA's and the considerably lower T_c for 2,6-dimethyl-PMAm may be observed over a wide range of the monomer concentration.

The numerical values of ΔH_{ss} and ΔS^0_{ss} evaluated from the slope and the intercept of the straight line are shown in Table 2, indicating that the dimethyl substitution mainly reduces the ΔH_{ss} value of PMAm, in contrast to the decrease in the ΔS^0_{ss} value of PMA [14], and that the T_c of PMAm is not changed by the o-monosubstitution. The lower ΔH_{ss} value for 2,6-dimethyl-PMAm may result from greater steric crowding in the polymer than in the monomer.

Since there are indications that bulkiness of the o-substituent critically affects the T_c of the PMA according to Eq. (1) [6], conformations of the PMAm and of their polymers in relation to steric hindrance
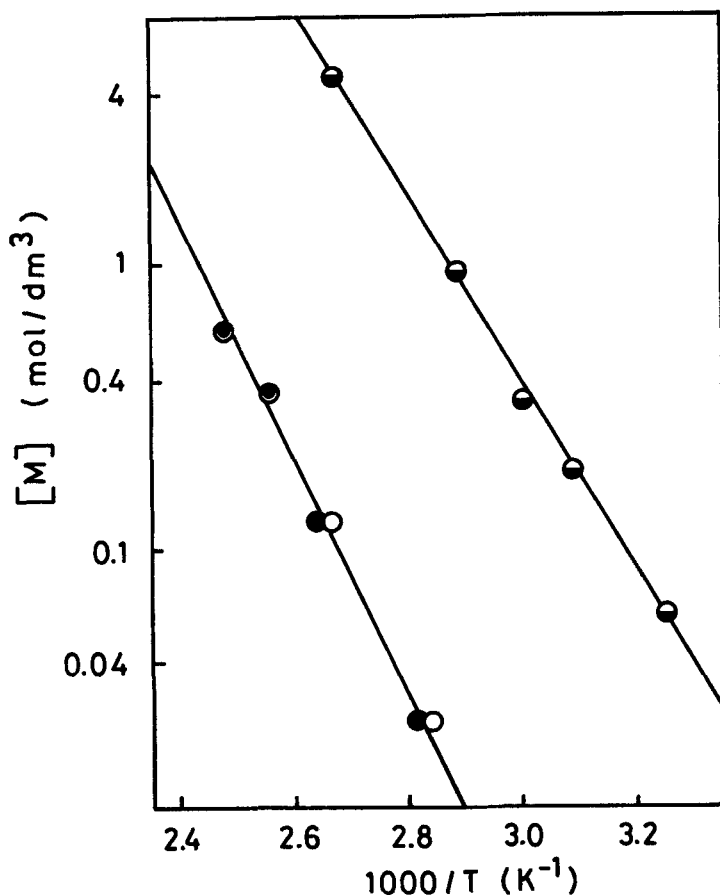
FIG. 2. Dependence on equilibrium monomer concentration of T_c in DMF: (○) PMAm, (●) o-methoxycarbonyl-PMAm, (◐) 2,6-dimethyl-PMAm.

were considered. The molecular models of the monomers and polymers show that the substituted benzene ring is almost perpendicular to the plane involving the carbonyl group in order to minimize the steric interaction between the substituent and the carbonyl oxygen. There is, however, general agreement that anilides tend to maintain the coplanarity of the ring with the amide plane [15], showing that the PMAm's may have the same tendency.

As can be seen from the ^{1}H-NMR spectra of o-methoxy-PMAm and the polymer from it (Fig. 3), the signal assigned to the o-proton appeared at a lower magnetic field than those due to the m- and p-protons,

TABLE 2. Enthalpy and Entropy Changes for Polymerization of Substituted PMAm in DMF

Substituent	ΔH_{ss}, kJ/mol	ΔS^{0}_{ss}, J/(K·mol)
None	-34.0	-82.4
o-Methoxycarbonyl	-34.0	-82.4
2,6-Dimethyl	-27.7	-79.5

because the o-proton in the plane of the carbonyl group is strongly de-shielded. The shift to lower field is regarded as supportive evidence for the coplanarity of the carboxanilide. The same behavior of the o-proton was observed even in the spectrum of the polymer, showing that the coplanarity of the carbonyl group and the ring holds in the polymer of the o-methoxy-PMAm. A similar deshielding effect was also found in the spectra of the other o-monosubstituted PMAm's and their polymers.

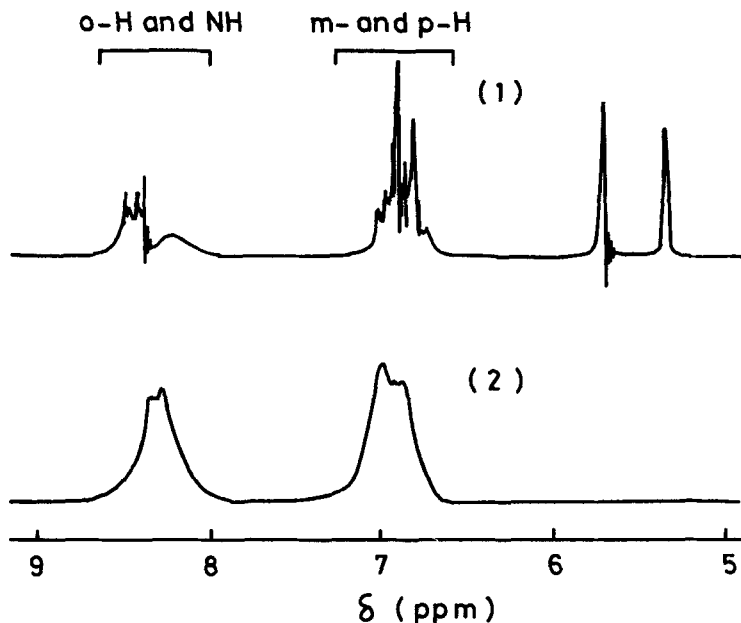FIG. 3. ^{1}H-NMR spectra of o-methoxy-PMAm (1) and poly(o-methoxy-PMAm) (2) in deuterochloroform.

In contrast to these findings, in the ^{1}H-NMR spectra of the o-monosubstituted PMA's, the signals due to the m-, o-, and p-protons appeared in a narrow range of chemical shift, as expected from the nonplanar conformation. Therefore, the different type of the o-substituent effect on PMAm polymerization from that on PMA polymerization may arise from a difference in conformation of the monomer or the polymer.

Generally, the lowering of T_c can be interpreted by an increase or decrease in stability of the monomer or the polymer [10]. An increase, rather than a decrease, in the stability of the monomer by o- and 2,6-disubstitutions could not be anticipated, and the IR, ^{1}H-NMR, and ^{13}C-NMR spectra of the monomers did not show any evidence for the considerable change of stability with respect to the carbon-carbon double bond. The main factor for decreasing T_c might lie in the polymer.

It seems to be possible that the o-substituent bound to the polymer with the coplanar carboxanilide group has little effect on T_c because of the more prominent effect of the rigid side group in determining T_c. In the case of poly(2,6-dimethyl-PMAm), however, mainly due to the steric requirement, the substituents force rotation of the ring around the C(O)–N bond to relieve steric hindrance as was the case for o-substituted or 2,6-disubstituted poly(PMA). This hypothesis could serve as an explanation for the constant T_c of the o-monosubstituted PMAm's and the considerable decrease in T_c by the 2,6-dimethyl substitution, results which are quite different from those observed for o-substitution of PMA's (as given by Eq. 1).

Reactivity of o-Substituted PMAm

The reactivities of the PMAm's (M_1) toward the polystyrene radical relative to styrene itself were calculated from the comonomer-copolymer composition relations given in Fig. 4. Table 3 summarizes the monomer reactivity ratios and the relative reactivity expressed by $1/r_2$. Because isolation of the copolymers of o-methyl-PMAm from the polymerization mixture was successful only in a limited range of comonomer composition, the relative reactivity of this monomer is given by a range of approximate values.

Monosubstitution, except for o-phenyl substitution, causes higher reactivity than PMAm by a factor of about 3 (Table 3). This is in contrast to what is expected by consideration of the lower reactivities of the PMA's, as in Eq. (2). The polar and resonance factors of the o-substituent are unlikely to have considerably effect on the stabilization of the transition state, as can be seen from the small sensitivity of p-substituted PMAm [16] and PMA [17] toward substituent change.

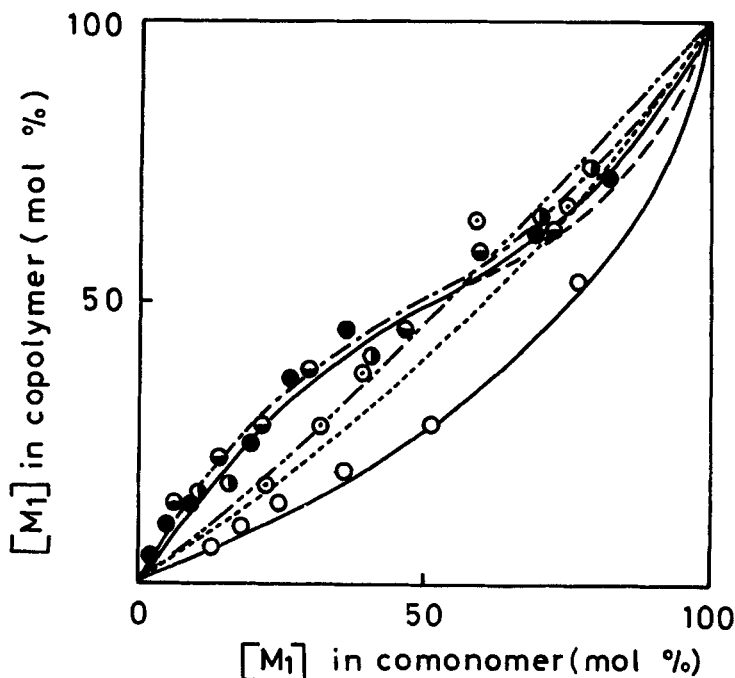The enhancement of the reactivity seems to be ascribable to steric

FIG. 4. Comonomer-copolymer composition relations for co-polymerizations of the o-substituted PMAm's (M_1) with styrene (M_2) in DMF: ($--$) M_1 = PMAm [16], (◑) o-methoxycarbonyl-PMAm, (⊛), o-phenyl-PMAm, (○) 2,6-dimethyl-PMAm, (◕) o-methoxy-PMAm, (●) o-chloro-PMAm.

factors. However, a blocking effect due to the o-substituent against an approaching growing polymer radical can only explain a decrease in reactivity in the homo- and copolymerization of the PMA's [6] but not an increase in the reactivity of PMAm. Resulting from the interaction of the carbon-carbon double bond and the carboxanilide group with the o-substituent in the same plane, the ground-state strain in the PMAm's might be partially relieved by the reaction proceeding from the double bond to the single bond. The increase in reactivity seems to be more important than the decrease by the blocking effect on the propagation of the o-monosubstituted PMAm's. This is the relevant interpretation for the enhanced reactivity. In the case of the PMAm having relatively large substituents, such as the o-phenyl group, the increase in reactivity is not so significant as the o-monosubstitution by the smaller group, indicating that the blocking effect against an approaching polymer radical

TABLE 3. Copolymerization of Substituted
PMAm (M_1) with Styrene (M_2)

Substituent	r_1	r_2	$1/r_2$
None[a]	0.71	1.42	0.70
o-Methoxy	0.45	0.49	2.04
o-Chloro	0.32	0.41	2.44
o-Methyl	-	-	2.0-2.5
o-Methoxycarbonyl	0.71	0.53	1.89
o-Phenyl	0.98	1.18	0.85
2,6-Dimethyl	0.20	1.84	0.54

[a]Reference 16.

becomes appreciable in the PMAm having the larger group. There-
fore, the lower reactivity for 2,6-dimethyl-PMAm than PMAm is
rationalized as a result of a more significant blocking effect by the
methyl groups.

Thermogravimetric Analyses

The thermograms in Fig. 5 show that these polymers degrade ther-
mally to the corresponding monomers with no residue remaining at
500°C or above. MDT's for the polymers of the substituted PMAm's
were found to be lower than that of poly(PMAm): MDT's for poly-
(PMAm), poly(o-phenyl-PMAm), poly(o-methyl-PMAm), and poly(2,6-
di-methyl-PMAm) were 438, 427, 408, and 415°C, respectively.
The considerably lower T_c for 2,6-dimethyl-PMAm is interpreted
by the greater crowding resulting in destabilization of the polymer, as
already described. If stability is the predominant factor for determin-
ing MDT of the polymer, poly(2,6-dimethyl-PMAm) would exhibit the
lowest MDT among the polymers examined. Because MDT's for the
polymers other than poly(PMAm) are in a narrow temperature range,
irrespective of the bulkiness of the substituent, MDT has turned out
to be more complicated than anticipated. It seems to be reasonable
that introducing the 2,6-dimethyl groups results in destabilization of
the polymer relative to the monomer, but in no facilitation of the cleav-
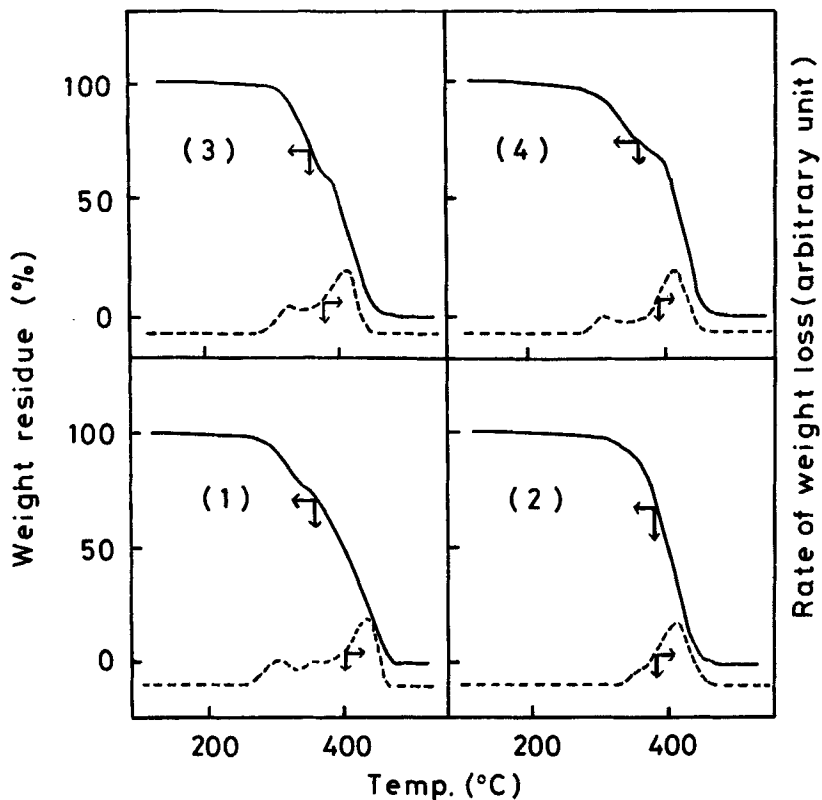age of the main chain.

FIG. 5. Thermogravimetric analysis (—) and differential thermo-gravimetric analysis (--) of poly(PMAm) (1), poly(o-phenyl-PMAm) (2), poly(o-methoxy-PMAm) (3), and poly(2,6-dimethyl-PMAm) (4).

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