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Syntheses of Polyamide-Poly(methyl methacrylate) Graft Copolymers by Polycondensation Reactions of Macromonomers

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Summary

Dicarboxyl-terminated macromolecular monomers (macromonomers) were synthesized by radical polymerization of methyl methacrylate in the presence of thiomalic acid as a chain transfer agent. This macromonomer and sebacic acid were condensed with diamines (p,p'-diaminodiphenyl ether, p,p'-diaminodiphenylmethane and m-phenylenediamine) by triphenylphosphite-pyridine system. Thus, graft copolyamides of well-defined structure and composition were readily prepared. This is the first example of the polycondensation reactions of macromonomers.

Introduction

Graft copolymers of well-defined structure and composition continue to be a subject of active interest in the syntheses of functionalized polymers. Especially, oligomers with polymerizable end groups, so-called macromonomers (macromolecular monomers) have been used for the preparation of the tailored graft copolymers.

Recently, we reported the syntheses and the characterization of the comb-type graft copolymers by radical copolymerization using macromonomers (ITO et al.,1980). The macromonomers were prepared by end capping the carboxyl group-terminated prepolymers with glycidyl methacrylate. On the other hand, Milkovich have reported the syntheses of macromonomers (macromer® as a registered trade name) and the preparation of thermoplastic graft copolymers (MILKOVICH 1980).

Thus, a number of vinyl-type macromonomers have been prepared by using functional initiators or end capping reagents (for example, ASAMI et al., 1980 and GOETHALS et al., 1981). However, only radical copolymerizations of macromonomers have so far been studied. Here we wish to extend the concept of macromonomers with vinyl-end-groups to those with dicarboxyl-end-groups, which may undergo condensation

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Scheme I

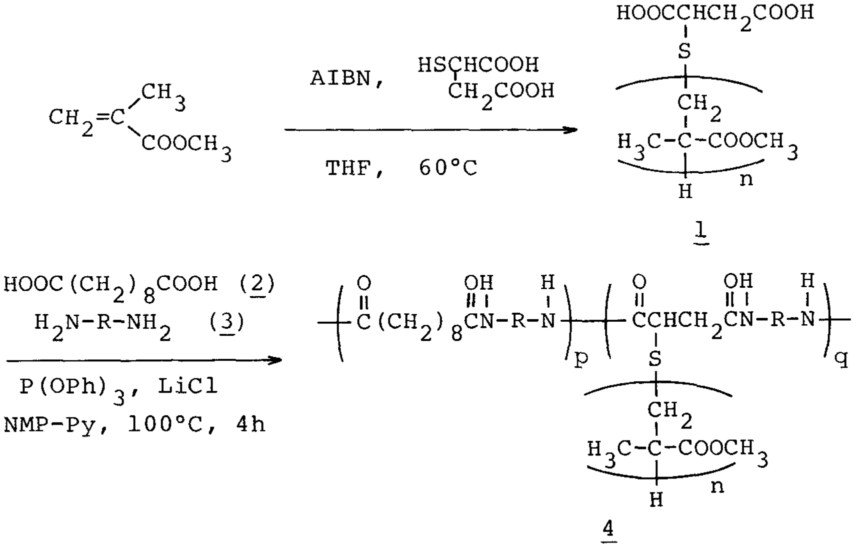


TABLE 1

Syntheses and Characterization of Macromonomers[a)]

Run	$[I]_0/[M]_0$ (10^{-3})	$[S]_0/[M]_0$ (10^{-2})	Time (h)	Yield (%)	$\bar{M}n(10^3)$ VPO	GPC[b)]	Tit[c)]	$\bar{M}w/\bar{M}n$	Cs[d)]
1	9.62	5.19	2.5	41	3.9	3.2	4.0	1.90	0.441
2	9.61	4.07	2.5	40	4.5	4.0	5.0	1.91	0.449
3	9.04	3.55	2.5	27	6.1	4.2	6.1	1.84	0.439
4	7.70	4.47	3.0	39	5.7	4.4	6.5	1.71	0.302
5	8.44	8.44	3.0	57	4.0	2.3	3.2	1.61	0.314
6	8.32	3.05	3.0	61	6.6	5.0	7.5	1.75	0.341

a) Reactions were carried out at 60°C in THF(tetrahydrofuran). [I]=[AIBN](α,α'-azobisisobutyronitrile), [S]=[TMA](thiomalic acid), [M]=[MMA] (methyl methacrylate).

b) Calculated by using calibration curve for polystyrene.

c) Determined by end-group titration assuming two carboxyl groups per molecule.

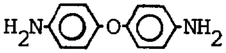
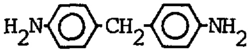
d) Calculated from $Cs=\log(1-\alpha[M]_0/n[S]_0)/\log(1-\alpha)$ α;conversion, n;degree of polymerization reaction with diamines. The present paper describes the syntheses of poly(methyl methacrylate) macromonomers and the polycondensation reactions with diamines resulting in the preparation of the well-defined graft copolyamides. Aromatic diamines were used to form the hard segment of graft copolymers.

Results and Discussion

The synthesis of graft copolymer was carried out according to Scheme I. Dicarboxyl group-terminated macromonomer(1) was prepared by radical polymerization of methyl methacrylate in the presence of thiomalic acid as a chain transfer agent. The results of the preparation of 1 are summarized in TABLE 1. 1 of a desired $\overline{M}n$ can be readily prepared by controlling the feed ratio of the monomer to the chain transfer agent in the case of the constant reaction temperature. Thus, various molecular weight samples were prepared by this method. IR spectrum of 1 is illustrated in Figure 1. Carbomethoxy group in 1 absorbs at 1720 cm^{-1}.

TABLE 2

Syntheses and Characterization of Graft Copolymers[a)]

Run	Diamine[b)]	Feed 1 ($\overline{M}n$)[c)]	 1 (mol%)[d)]	 MMA (wt%)	Polymer PMMA[e)] (mol%)[d)]	 MMA[e)] (wt%)	 $\eta_{sp/c}$[f)]
1		6100	2.40	26.3	1.54	19.9	0.62
2	〃	6450	4.00	38.6	2.78	32.4	0.69
3	〃	6450	1.20	15.8	0.78	11.8	1.35
4	〃	3200	2.40	15.4	1.56	11.3	1.34
5		6450	2.40	27.5	1.67	22.4	0.63
6		6450	2.40	32.9	1.64	27.3	0.78

a) Reactions were carried out at 100°C in NMP(N-methylpyrrolidone)(20ml) and pyridine(5ml). [P(OPh)$_3$]/[diamine]=1, [LiCl]=4wt%
b) 5.00 mmol was used.
c) Calculated by end-group titration.
d) mol% of 1; [1]/([1]+[2])×100
e) Calculated from ^1H-NMR.
f) Measured in conc. H_2SO_4 at 30°C. c=0.5g/dl

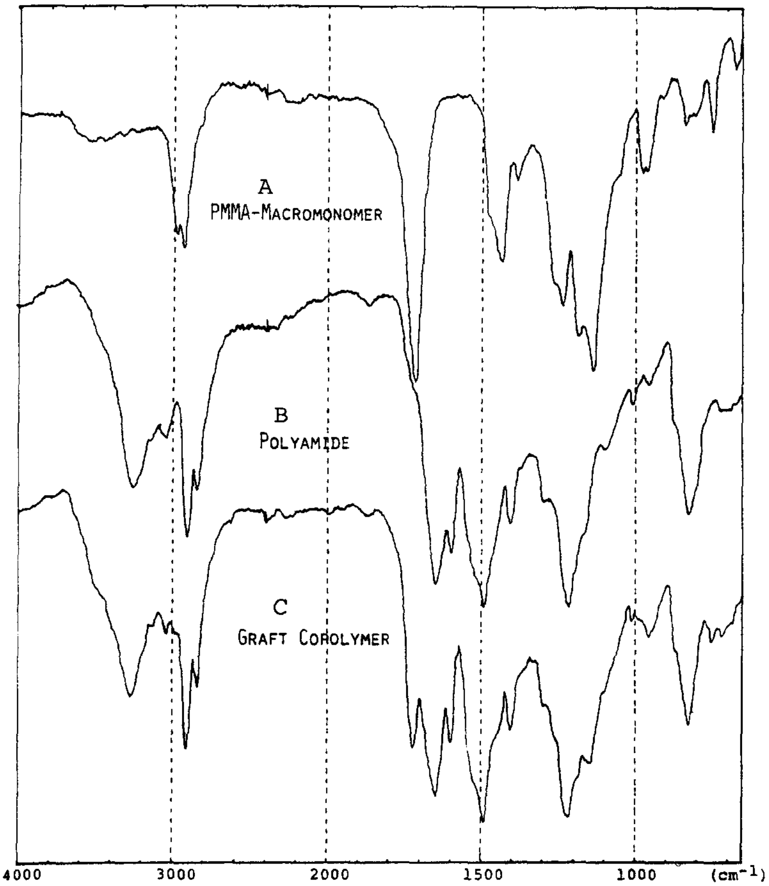


Figure 1. IR spectra of PMMA-macromonomer(A)(1), polyamide(B) and graft copolymer(C) (4) (KBr).

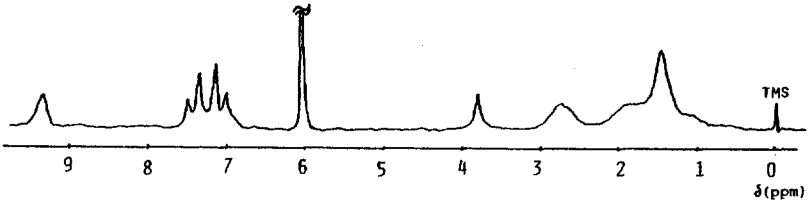


Figure 2. ^{1}H-NMR spectrum of graft copolymer (4) (in CF_3COOH and $Cl_2CHCOOH$)

The macromonomer(1) and sebacic acid(2) were condensed with p,p'-diaminodiphenyl ether(3) by triphenylphosphite-pyridine system (HIGASHI et al., 1980). The total amount of dicarboxyl monomers (1 and 2) should be equal to that of the diamine(3). The results of the preparation of the graft copolymers(4) are summarized in TABLE 2. IR spectrum of the graft copolymer (Run 1 in TABLE 2) is shown in Figure 1 together with macromonomer(1) and polyamide which contains no 1 for comparison. This result supports the composition of 4. Figure 2 illustrates ^{1}H-NMR spectrum of 4 (Run 4 in TABLE 2). The wt% of MMA in 4 was calculated from the integral ratio of the aromatic protons (δ 6.9-7.6 ppm) to $-OCH_3$ protons (δ 3.8 ppm) or the ratio of $-OCH_3$ protons to $-CH_2-$ and $-CH_3$ protons (δ 0.8-3.1 ppm). These results were supported by their elemental analyses (see Experimental section). Since the reprecipitation and the washing removed the low molecular weight polyamides, which were appreciably grafted with PMMA, the decrease of wt% of MMA in copolymers was observed.

Relatively high molecular weight copolymers were obtained by using aromatic diamines such as 3. Similarly, p,p'-diaminodiphenylmethane and m-phenylenediamine were used in place of 3 (Runs 5 and 6 in TABLE 2). Polyamides of aromatic diamines may be expected to form the hard segment of graft copolymers. The studies of physical properties of graft copolymers are now under investigation.

Experimental section

Materials

Commercial MMA was distilled under vacuum. AIBN was recrystallized from methanol. Sebacic acid, thiomalic acid, p,p'-diaminodiphenyl ether, p,p'-diaminodiphenylmethane and m-phenylenediamine were commercially available and used without further purification. NMP was dried over molecular sieves and distilled. Pyridine, benzene and THF were distilled over CaH_2 and Na, respectively.

Macromonomers(1)

In a glass ampule, MMA, thiomalic acid, AIBN and THF were placed and sealed under vacuum. Polymerization was carried out at 60°C for 2.5-3.0 hours. The macromonomer was precipitated into petroleum ether, purified twice by reprecipitation from benzene into petroleum ether, once from acetone into water, then dried under vacuum. The carboxyl-group content was determined by titrating the polymer in THF with 0.02N aqueous potassium hydroxide, using phenolphthalein as an indicator.

Graft Copolymers(4)

Under nitrogen, a mixture of macromonomer(1), sebacic acid, diamine(3), triphenylphosphite, LiCl, pyridine and NMP was placed in a flask equipped with a reflux condenser and heated at 100°C for 4 hours. The resulting reaction mixture was poured into methanol. The polymer was obtained almost quantitatively and purified by reprecipitation from dichloroacetic acid into water-methanol (1:1 V/V) and drying in vacuo. As a typical example, the elemental analysis of 4 (Run 2 in TABLE 2) is C 67.27%, H 7.38%, N 4.87% and O 20.48%. This result is in fair agreement with that calculated from the ^{1}H-NMR spectrum (C 67.46%, H 7.41%, N 4.93% and O 20.21%).

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