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Reactions

High Molecular Weight Poly(Methyl Alkyl Fumarates): Radical High Polymerization of Methyl Alkyl Fumarates and Monomer-Isomerization Radical Polymerization of Methyl Alkyl Maleates*

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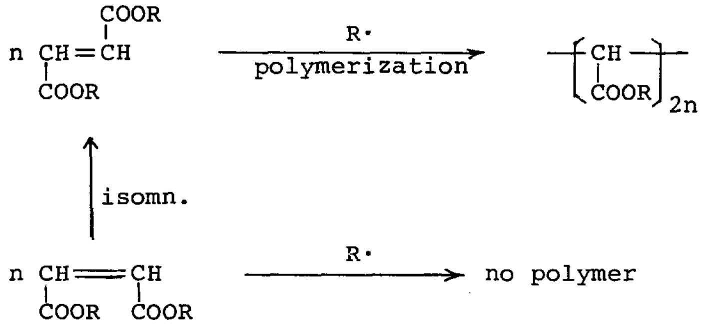
Summary

High molecular weight poly(methyl alkyl fumarate) were prepared through radical polymerization of methyl alkyl fumarates(MRF) and monomer-isomerization radical polymerization of methyl alkyl maleates(MRM). The polymerization reactivities(yield and viscosity) of MRFs and MRMs were found to increase with increasing of the bulkiness of the ester alkyl substituents, but MRFs showed generally higher reactivities than MRMs. These polymers were also observed to consist of less- or non-flexible rod-like poly(methoxycarbonylmethylene-alt-alkoxycarbonylmethylene) structure depending on their bulkiness. The MtBF polymer did not melt, which showed somewhat decreased thermal stability.

Introduction

In previous papers[OTSU et al., 1981b, 1981d], dialkyl fumarates(DRF) were found to homopolymerize in the presence of radical initiator to give high molecular weight polymers. Similar polymers were also obtained from monomer-isomerization radical polymerization of dialkyl maleates(DRM) in the presence of both radical initiator and isomerization catalyst such as morpholine, as is shown in Eq.(1)[OTSU et al., 1981a, 1981c, 1983 and TOYODA et al., 1983a];



(1)

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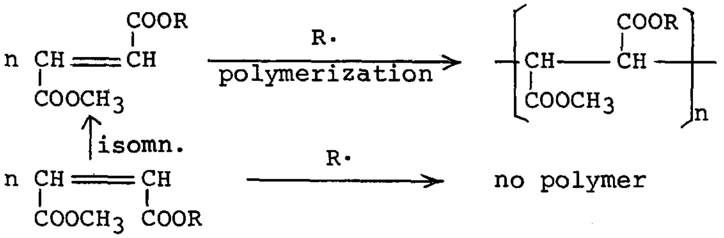
[*] Polymers from 1,2-Disubstituted Ethylenic Monomers. VIII.

These polymers obtained from both DRFs and DRMs were confirmed to consist of a poly(alkoxycarbonylmethylene) structure, which is produced by ordinary vinylene polymerization mechanism[OTSU et al., 1981b, 1981d].

If methyl alkyl fumarates(MRF) and methyl alkyl maleates (MRM) are used and homopolymerized via an ordinary head-to-tail propagation(Eq.2), the products correspond to an alternating copolymers, poly(methoxycarbonylmethylene-alt-alkoxycarbonylmethylene);



$$\begin{array}{ccc} n\,\underset{COOCH_3}{CH}=\overset{COOR}{CH} & \xrightarrow[\text{polymerization}]{R\cdot} & \left[\underset{COOCH_3}{CH}-\overset{COOR}{CH}\right]_n \\ \Big\uparrow \text{isomn.} & & \\ n\,\underset{COOCH_3}{CH}=\underset{COOR}{CH} & \xrightarrow{R\cdot} & \text{no polymer} \end{array} \qquad (2)$$

It is of interest to clarify the monomer structure-reactivity and the polymer structure-property relationships of these new monomers and polymers. In the present paper, the results of radical high polymerization of MRFs and of monomer-isomerization radical polymerization of MRMs are described. Some thermal properties of the resulting polymers are also given. The monomers used in this paper are R= C_2H_5(MEF or MEM), R= n-C_3H_7(MnPF or MnPM), R= i-C_3H_7(MiPF or MiPM), R= n-C_4H_9(MnBF or MnBM), R= i-C_4H_9(MiBF or MiBM), R= s-C_4H_9(MsBF or MsBM), R= t-C_4H_9(MtBF) and R= t-C_5H_{11}(MtAF) in Eq.(2).

Experimental

MRF Monomers

All of these monomers were synthesized as follows: Maleic anhydride was reacted with methanol, and the resulting monomethyl maleate was then reacted with thionyl chloride in benzene. The fumaroyl chloride monomethyl ester obtained was allowed to react with the respective alcohols in the presence of the catalytic amount of pyridine in dry diethyl ether. The resulting MRF monomers were purified by repeated distillation in a stream of nitrogen. These monomers were confirmed to be pure from ^{1}H-NMR and gas chromatographic analyses.

MRM Monomers

Monomethyl maleate obtained above was esterified with the respective alcohols in the presence of p-toluenesulfonic acid in benzene. The resulting MRMs were purified repeateadly by fractional distillation under reduced pressure. The purities of MRMs obtained were confirmed to be above 98% by gas chromatography(column: PEG-6000).

Other Reagents

2,2'-Azobisisobutyronitrile(AIBN) was recrystallized from methanol. Solvents and precipitants(non-solvents) were used after ordinary purification.

Polymerization

Bulk polymerizations of MRFs and MRMs were carried out in a degassed glass tubes in the presence of AIBN and AIBN-morpholine, respectively, at 60°C. After polymerization for a given time, the content of the tubes was poured into a large amount of n-hexane to precipitate the polymer, which was washed several times with n-hexane, and then dried under vacuum.

Characterization

The structure of the polymers obtained was confirmed by IR, ^{1}H-NMR and ^{13}C-NMR spectra. The intrinsic viscosities, $[\eta]$ of the polymers were measured viscometrically in benzene at 30°C. The softening temperature and thermal degradation temperature were determined by micromelting apparatus and thermogravimetric analysis(heating rate 10°C/min., in N_2), respectively.

Results and Discussion

Radical Homopolymerization of MRFs

The results of bulk polymerization of MRFs with AIBN are shown in Table 1, in which those of the DRFs are also indicated for comparison.

Here, all of MRFs used are found to homopolymerize under usual conditions. When the polymerization reactivities(polymer yield and $[\eta]$) are compared with DRFs which

Table 1 Radical Homopolymerization of MRFs and DRFs[a)]

MRF	Yield (%)	$[\eta]$ (dl/g)	DRF	Yield (%)	$[\eta]$ (dl/g)
MEF	4.8	0.10	DEF	10.0	0.20
MnPF	4.3	0.10	DnPF	5.8	0.13
MiPF	10.4	0.21	DiPF	29.1	0.86[e)]
MnBF	4.0	0.08	DnBF	6.4	0.15
MdBF	7.8	0.16	DsBF[c)]	16.4	0.41
MiBF	2.5	—	DiBF	5.4	0.12
MtBF[b)]	23.5	0.45	DMF[d)]	10.5	0.05
MtAF	13.2	0.35	DEF[d)]	33.4	0.10

[a)] Polymerization conditions: [AIBN]= 20 mmol/l in bulk at 60°C for 10 hours.

[b)] Data for MtBF reported previously(TOYODA et al., 1983b).

[c)] Polymerized for 12 hours.

[d)] Polymerized in benzene at 90°C for 4 hours; [DMF]= 5.3, [DEF]= 5.2 mol/l.

[e)] Number-average molecular weight was 110,000.

have identical R substituent, MRFs except MtBF and MtAF show lower reactivities than those of the DRFs, i.e. MRFs homopolymerize with the intermediate reactivities between DRFs and DMF which had the lowest reactivity[OTSU et al., 1981d].

It is interesting to note that when the bulkiness of the propyl or butyl ester substituents in both MRFs and DRFs increases, the polymerization reactivities increase, as in the following order:

In MRF series: MnPF $\ll$ MiPF; MnBF $\simeq$ MiBF $<$ MsBF $\ll$ MtBF

In DRF series: DnPF $\ll$ DiPF; DnBF $\simeq$ DiBF $<$ DsBF

It is also marked that MtBF and MtAF with bulky substituent as well as DiPF homopolymerize quite easily to give high number-average molecular weight($\bar{M}_n$) over ca. 50,000 which has been roughly estimated on the basis of the $\bar{M}_n$-$[\eta]$ relation for poly(DiPF)[OTSU et al., 1983]. These polymers were found to form a transparent film by casting from their benzene or toluene solution.

Monomer-Isomerization Radical Polymerization of MRMs

In previous papers[OTSU et al.,1983a; TOYODA et al., 1983a], DMM and DEM were found to polymerize in the presence of AIBN and morpholine via a monomer-isomerization radical polymerization to give poly(DMF) and poly(DEF), respectively. Some MRMs were also observed to undergo these polymerization[OTSU et al., 1981c]. The results of radical polymerization of MRMs including new monomers are shown in Table 2, in which those of DRMs are also indicated for comparison.

Table 2 Monomer-Isomerization Radical Polymerization of MRMs and DRMs

MRM[a]	Yield (%)	$[\eta]$ (dl/g)	DRM[b]	Yield (%)	$[\eta]$ (dl/g)
MEM	11.0	0.02	DMM	8.2[c]	0.01
MnPM	2.0	—	DEM	6.2[d]	0.10
MiPM	10.4	0.05	DiPM	25.1[e]	0.25
MnBM	1.4	—	DnBM	trace	—
MsBM	1.5	—	DEHM[f]	8.3	—

[a] Polymerization conditions: [AIBN]= 20 mmol/l,[Morph.] = 115 mmol/l in bulk at 60°C for 20 hours.

[b] Polymerization conditions: [AIBN]= 10 mmol/l,[Morph.] = 115 mmol/l in bulk at 60°C for 20 hours[OTSU et al., 1981c].

[c] Polymerized with azobiscyclohexanecarbonitrile at 90°C for 8 hours([DMM]= 5.3 mol/l in benzene).

[d] Polymerized for 10 hours.

[e] Polymerized for 15 hours.

[f] DEHM: diethylhexyl maleate.

From this table, the polymerization reactivities for MRMs were lower than those of DRFs in a similar manner of fumarate monomers(Table 1), but those for both maleate monomers were also less reactive than the respective fumarate monomers. However, it is noted that MiPM whose trans isomer, MiPF, was homopolymerized readily(Table 1), also underwent easily monomer-isomerization radical polymerization.

Characterization of the Polymers

The polymers obtained from both MRFs and MRMs were white powder and soluble in benzene, chloroform and tetrahydrofuran. The ^{13}C-NMR spectra of the polymers from MiPF and MiPM, as an example, are shown in Fig. 1, from which both polymers were found to consist of an identical structure, poly(methoxycarbonylmethylene-alt-isopropoxycarbonylmethylene), as shown in Eq.(2). Similar results were also observed for the other polymers obtained from MRFs and MRMs, poly(methoxycarbonylmethylene-alt-alkoxycarbonylmethylene)s. These observations were the same as those found for DRFs and DRMs[OTSU et al., 1983a; TOYODA et al., 1983a].

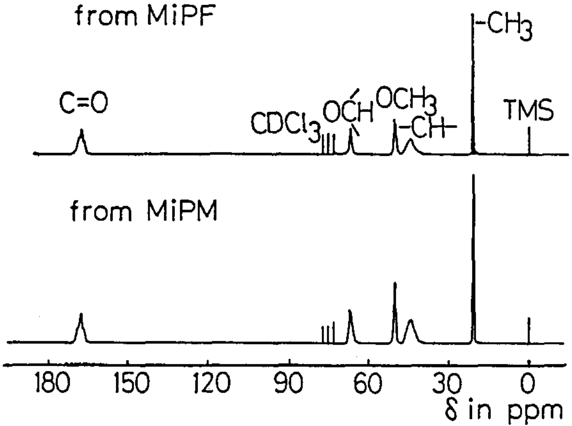


Fig. 1 ^{13}C-NMR spectra of the polymers from MiPF and MiPM in deuterochloroform

From considerations by means of molecular model, these polymers are assumed to consist of less- or non-flexible rodlike structure. The rigidity depends on the bulkiness of the ester alkyl groups in the MRF polymers. Namely, when the bulky ester alkyl groups were substituted in the polymers of MRF and DRF, the polymer chain became more rigid[OTSU et al., 1981d; TOYODA et al., 1983b], and these polymers did not melt on heating.

Table 3 summarizes the thermal properties of the MRF polymers. The apparent softening and glass transition temperatures are observed to increase with increasing of

Table 3 Thermal Properties of the Homopolymers of MRFs

Homopoly-mers from	Softening temp. (°C)[a]	Degradation temp. (°C)		Residue at 500°C (%)
		Initial	Maximum	
MEF	132-140(45)	229	378	6.4
MnPF	106-110(22)	225	377	8.0
MiPF	———	220	335	15.6
MnBF	63 - 67(8)	218	372	7.6
MsBF	———	216	329	22.8
MiBF	87 - 93(48)	210	372	4.8
MtBF	———	196	226(322)	19.7

[a] Values in parentheses indicate the apparent glass transition temperature determined by DSC.

the bulkiness of the ester alkyl groups, i.e. the rigidities of the polymer chain, but the bulky MiPF, MsBF and MtBF polymers did not melt before degradation. Similar results were also observed for the bulky DiPF and DtBF polymers[OTSU et al., 1983b].

From Table 3, thermal degradation temperature and the amount of the residue at 500°C of the MRF polymers were also dependent on the bulkiness of the ester alkyl groups.

More detailed results will be described in future.

References

OTSU, T. and TOYODA, N.: Makromol. Chem., Rapid Commun., 2, 79(1981a)

OTSU, T. ITO, O. and TOYODA, N.: Makromol. Chem., Rapid Commun., 2, 725(1981b)

OTSU, T., ITO, O. and TOYODA, N.: Makromol. Chem., Rapid Commun., 2, 729(1981c)

OTSU, T., ITO, O. TOYODA, N. and MORI, S.: Mem. Fac. of Eng., Osaka City Univ., 22, 129(1981d)

OTSU, T., ITO, O. and TOYODA, N.: J. Macromol. Sci.-Chem., A19, 27(1983a)

OTSU, T., YASUHARA, T., FUKUSHIMA, K. and TOYODA, N.: Polymer Preprints, Jpn., 32, (1983b)

TOYODA, N., YOSHIDA, M. and OTSU, T.: Polymer J., 15, 255 (1983a)

TOYODA, N. and OTSU, T.: J. Macromol. Sci.-Chem., A19, 1011(1983b)

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