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Synthesis of high molecular weight poly(dialkyl fumarate)s bearing *n*-alkyl side chains from poly(di-*tert*-butyl fumarate) via olefin elimination and reesterification in a one-pot

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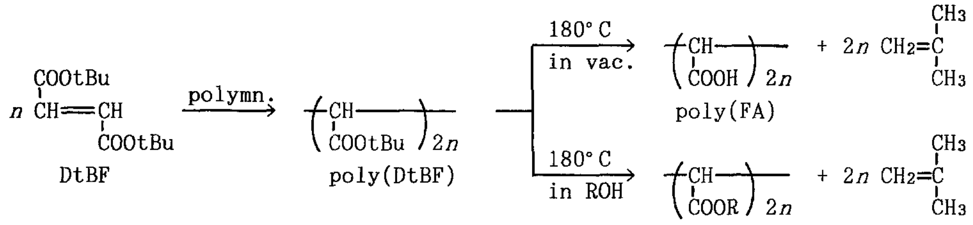
SUMMARY

High molecular weight poly(dialkyl fumarate)s bearing *n*-alkyl esters such as an octadecyl group were prepared efficiently from poly(di-*tert*-butyl fumarate) by the one-pot synthesis, i.e. both elimination of isobutene from the *tert*-butyl ester and the subsequent esterification were performed in a corresponding alcohol at 170-180°C in a one-pot without isolating poly(fumaric acid). The resulting polymers were characterized by IR and NMR spectroscopies and GPC. The polymers with various contents of an octadecyl group in the side chain were also obtained similarly from the copolymer of di-*tert*-butyl fumarate with diisopropyl fumarate.

INTRODUCTION

It has been reported that dialkyl fumarates (DRF) with a bulky alkyl group polymerize easily to give high molecular weight poly(DRF)s consisting of a less-flexible poly(substituted methylene) structure [2-7]. Among DRFs examined, di-*tert*-butyl fumarate (DtBF) showed the highest polymerization reactivity [4,5], whereas DRF with primary alkyl ester groups was found to have a lower polymerization reactivity than DtBF.

In the previous papers [4-7], poly(DtBF) was reported to be converted into poly(fumaric acid) (poly(FA)) by heating at 180°C under vacuum or in a solution via elimination of isobutene from the ester group (Scheme I).



Scheme I

If re-esterification of the resulting poly(FA) is possible, poly(DRF)s modified by substitution of various ester groups will be obtained. However, poly(FA) is soluble only in alkaline water, and insoluble in any organic solvents, indicating that the conditions for esterification are limited, e.g. a strong alkylating reagent such as diazomethane is required. Therefore, it is proposed that poly(DtBF) is heated directly in *n*-alkyl alcohols such as octadecyl alcohol without isolating poly(FA), i.e. both the elimination of isobutene and esterification are performed in a one-pot (Scheme I). In this paper, the results of investigation on synthesis and characterization of the polymer consisting of a less-flexible poly(DRF) main chain and a flexible alkyl side chain are reported.

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EXPERIMENTAL

Dioctadecyl fumarate (DODF) and isopropyl octadecyl fumarate (iPODF) were prepared from fumaric dichloride and from its mono(acid chloride) of monoisopropyl ester with octadecyl alcohol, which were recrystallized from acetone and ethanol, respectively; DODF: mp 71.5°C, iPODF: mp 31°C.

Polymerizations were carried out in bulk or in benzene in the presence of 2,2'-azobisisobutyronitrile (AIBN) or 1,1'-azobiscyclohexane-1-carbonitrile (ACN). The one-pot synthesis of poly(DRF) from poly(DtBF) was performed in a corresponding alcohol in the presence of *p*-toluenesulfonic acid (PTS) in a nitrogen atmosphere. The polymer was precipitated with methanol or ethanol. In the case of poly(DODF), the resulting polymer was purified by extracting with ethanol to remove an unreacted octadecyl alcohol by means of a Soxhlet apparatus, and then reprecipitated from benzene and ethanol.

The composition in the copolymers was determined by ^{1}H NMR spectroscopy, and monomer reactivity ratio was calculated by a nonlinear least-squares method. Gel permeation chromatography (GPC) was carried out with THF as an eluent, and calibrated with standard polystyrenes. NMR spectra were taken using $CDCl_3$ and tetramethylsilane as a solvent and an internal standard, respectively.

RESULTS AND DISCUSSION

Hydrolysis of poly(DRF)

Poly(DtBF) and poly(diisopropyl fumarate) (poly(DiPF)) were attempted to hydrolyze under various conditions, but quantitative hydrolysis could not be accomplished; e.g. PTS/benzene/reflux/20 h, NaOH/THF-methanol/reflux/20 h, or conc.H_2SO_4/r.t./3 days. Hydrolysis of poly(diethyl fumarate) (poly(DEF)) did not also completely occur even in a homogeneous methanol solution by an acidic and alkaline catalysts, although it was reported that poly(DEF) partly hydrolyzed in conc.H_2SO_4 [8].

However, the copolymer of DiPF with methyl methacrylate (MMA) (DiPF 5.4 mol% in the copolymer) was soluble in conc.H_2SO_4 and hydrolyzed at a room temperature after a few days, and then methylation by diazomethane gave a copolymer of dimethyl fumarate and MMA. It suggests that the high resistance of poly(DRF) against hydrolysis comes from a poly(substituted methylene) structure, in which a carbonyl group is surrounded with hydrophobic alkyl groups [3,5]. Thus difficulty of the preparation of poly(FA) by hydrolysis of poly(DRF) exhibits a contrast to the quantitative formation of poly(FA) by the thermolysis of poly(DtBF) reported [4-7].

One-pot synthesis of poly(DRF)

The one-pot synthesis of poly(DRF)s with various alkyl groups from poly(DtBF) was carried out. The results are shown in Tab. 1. The poly(DRF)s with long-alkyl side chains were obtained with high yields in the presence of PTS, especially in the case of poly(DODF). In the absence of PTS, the yield of the poly(DODF) isolated was found to decrease. When the reaction was carried out in alcohols with a low boiling point such as *n*-hexanol, the resulting poly(DRF)s were recovered in a low yield. It suggests the formation of a methanol-soluble polymer on account of the incomplete esterification.

From the results of GPC measurement, the poly(DRF)s obtained in this study were confirmed to have high molecular weight as well as the starting poly(DtBF), although the high molecular weight poly(DRF)s bearing primary alkyl esters could not be obtained directly from polymerization (Tab. 1).

Tab. 1 One-pot Synthesis of High Molecular Weight Poly(DRF) from Poly(DtBF)

Alkyl group	One-pot synthesis from poly(DtBF)[a]					Polymerization of DRF[b]			
	Temp. (°C)	Time (h)	Yield[c] (g)	$\bar{M}_n$[d] x 10^{-4}	$\bar{M}_w/\bar{M}_n$[d]	[ACN] (mol/L)	Time (h)	Yield (%)	$\bar{M}_n$[d] x 10^{-4}
$(CH_2)_6H$	157	5	0.079(39)	2.9	2.4	0.02	10	12.6	0.9
$(CH_2)_7H$	176	5	0.174(87)	-	-	-	-	-	-
$(CH_2)_{12}H$	170	10	0.270(135)	5.9	1.9	-	-	-	-
$(CH_2)_{18}H$	180	10	0.368(184)	6.7	2.1	0.01	20	15.6	1.1
			0.080(40)[e]	5.1[e]	2.0[e]				
$-CH_2\underset{CH_2CH_3}{CH}(CH_2)_4H$	180	5	0.108(54)	4.1	1.9	0.02	10	7.8	(0.08)[f]

[a] Poly(DtBF) 0.2 g ($\bar{M}_n$ = 5.3 x 10^4 by GPC), alcohol 10 mL, in the presence of PTS in a nitrogen stream. [b] Polymerized in bulk at 80°C. [c] Values in parentheses indicate yield in % based on the weight of poly(DtBF) used. [d] By GPC. [e] In the absence of PTS. [f] [η] (dL/g) in benzene at 30°C.

In the ^1H and ^{13}C NMR spectra of poly(DODF) obtained from the one-pot synthesis, no *tert*-butyl group was detected (Fig. 1), and they were the same as those obtained from the direct polymerization. In the IR spectra (Fig. 2), the absorption band of carbonyl groups indicates an existence of carboxylic anhydride in the polymer reacted for a long period. It was estimated from the results of elementary analysis that an octadecyl group was introduced to the polymer over 90 mol% yield after the reaction for 10 h. The residual moieties were probably considered to be an acid or anhydride, and the latter may be formed by eliminations of water or octadecyl alcohol from a carboxylic acid and an octadecyl ester. In Fig. 3, the GPC elution curves of poly(DODF) obtained from poly(DtBF) are shown as a function of the reaction time. The polymer recovered after reacted for 0.5 h was insoluble in THF, indicating that the esterification was insufficient. The apparent molecular weight of poly(DODF) seemed to become almost constant after 5 h. A remarkable increase in the molecular weight of poly(DODF) did not observed compared with that of the poly(DtBF) used, i.e. from 5.3 x 10^4 to 6.7 x 10^4 by GPC, although the polymer yield was much high (184 %) by introduction of the octadecyl group into the side chain. It can be interpreted by the change in the rigidity of the poly(DRF) [5,9], and by alteration of the polymer shape, i.e. from linear to comb-like.

This method was applied to not only *n*-alkyl esters, but also ethyl ester by using an autoclave at 180°C. It was also found that the reaction in ethylene glycol or polyethylene glycol gave polymers insoluble in any solvents, but when diethylene glycol monomethyl ether and poly(ethylene glycol) monomethyl ether were used, the resulting polymers were soluble in water and alcohols.

Application to copoly(DtBF-DiPF)

The results of the application of introduction of an octadecyl group to copoly(DtBF-DiPF) are summarized in Tab. 2. Since both the monomer reactivity ratios of DiPF and DtBF were almost unity (Fig. 4), the content of

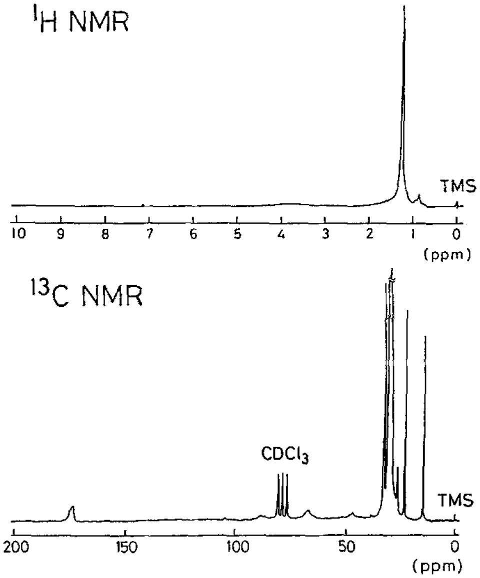

Fig. 1 ^1H and ^{13}C NMR spectra of poly(DODF) prepared from poly(DtBF).

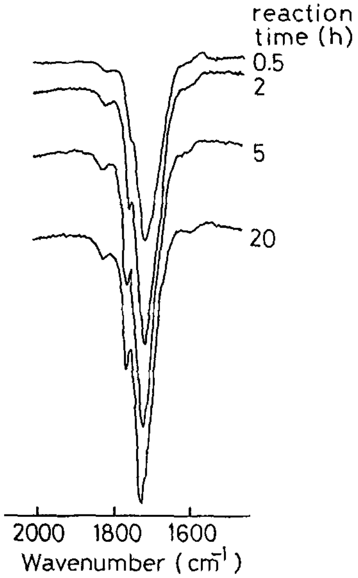

Fig. 2 IR spectra of poly(DODF) prepared from poly(DtBF).

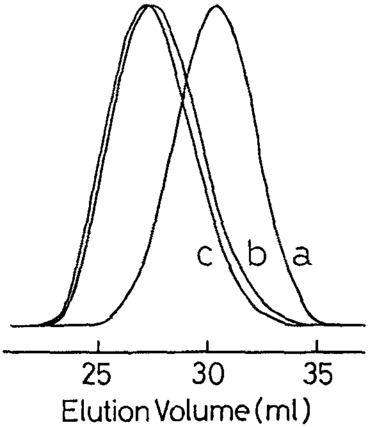

Fig. 3 GPC curves of poly(DODF) prepared from poly(DtBF); reaction time (a) 2 h, (b) 5 h, (c) 20 h.

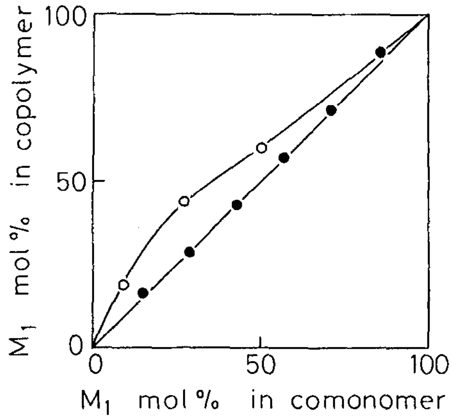

Fig. 4 Copolymerization composition curves for radical copolymerization at 60°C: DiPF(M_1)-DtBF(M_2)(●) $r_1=r_2=1$, DiPF(M_1)-DODF(M_2)(○) $r_1=1.07$, $r_2=0.33$.

Tab. 2 Introduction of an Octadecyl Group into Copoly(DtBF-DiPF)[a]

Copoly(DtBF-DiPF)[b] used					Yield (%)	Octadecyl group[d] (mol%)	$\bar{M}_n$[c] x 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]
[DtBF] in feed(mol%)	Time (h)	Yield (%)	$\bar{M}_n$[c] x 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]				
27.3	7	45.3	7.7	2.4	74	64	8.2	2.0
46.8	6	59.6	6.3	3.4	92	79	8.6	2.3
67.2	5	67.0	7.4	3.0	79	79	8.1	2.3

[a] Copolymer 1 g, octadecyl alcohol 10 g, PTS, in a nitrogen stream, at 170° C, for 10 h. [b] In bulk, [ACN] = 0.01 mol/L at 80° C. [c] By GPC. [d] From elementary analysis.

the DtBF unit in the copolymer is assumed to be almost equal to that in the comonomer. After reacted in octadecyl alcohol, the amount of the octadecyl group introduced were found to be higher than expected, as shown in Tab. 2. The anhydride formed during the reaction seemed to react further with octadecyl alcohol, giving the higher contents of an octadecyl group introduced than the contents of the *tert*-butyl ester of the copolymers. Because poly(DiPF) does not reacted in octadecyl alcohol, it is concluded that direct transesterification between isopropyl and octadecyl esters is negligible. When copoly(DtBF-DiPF) was heated under vacuum in the absence of alcohol at 180° C for 5 h, the weight-loss observed was greater than theoretical one which was calculated based on the quantitative elimination of isobutene [10]. The elimination of isopropanol from the isopropyl ester and the neighboring carboxylic acid which was generated from *tert*-butyl ester was confirmed by the absorption of carboxylic anhydride in the IR spectrum. In addition, isobutene and isopropanol were collected as the main volatiles.

Polymers bearing both isopropyl and octadecyl ester groups could be also obtained from copolymerization of DiPF with DODF or homopolymerization of iPODF as shown in Tab. 3. However, the copolymerization rate and molec-

Tab. 3 Copolymerization of DiPF(M_1) with DODF(M_2) in Bulk at 80° C

M_1 mol% in feed	[ACN] (mol/L)	Time (h)	Conv. (%)	$\bar{M}_n$[a] x 10^{-4}	M_1 mol% in copolymer
0	0.01	20	15.6	1.1	0
9.1	0.02	10	2.1	0.6	18.5
26.8	0.02	10	4.6	0.7	43.6
49.7	0.02	10	4.1	1.1	60.1
100	0.01	5	50.4	7.7[b]	100
-[c]	0.01	50	39.5	4.1	-

[a] By GPC. [b] By membrane osmometry. [c] Homopolymerization of iPODF with AIBN at 60° C.

ular weight of the copolymers were much lower than those for polymerizations of not only DiPF, but also DODF. From the composition curve for the copolymerization in Fig. 4, it is clear that DODF (M_2) has a lower monomer reactivity than DiPF (M_1) (r_1 = 1.07, r_2 = 0.33). From homopolymerization of iPODF, a high molecular weight polymer ($\bar{M}_n = 4 \times 10^4$) was obtained, but its polymerization rate was not so high and the content of the octadecyl group in the polymer was fixed to the 50 mol%.

Thermal property of the polymers

The polymers obtained in this work are a new type of polymers which have a rigid poly(substituted methylene) in the main chain and a flexible polymethylene in the side chain. The thermal property of the poly(DODF) obtained by the both methods, one-pot synthesis from poly(DtBF) and polymerization of DODF, was characterized and compared. Transparent and relatively flexible films were obtained from the solution of the poly(DODF) prepared from poly(DtBF), whereas the polymer from DODF was powdery because of its low molecular weight. The both polymers were observed to melt at 50-65°C, when they were heated on a hot plate. In the DSC thermogram of the latter sample on heating, an endothermic peak was observed at 59°C, agreeing with the results in literature [11]. On the other hand, poly(DODF) prepared from poly(DtBF) gave a broad transition peak at a lower temperature range. It might result from the difference in the molecular weight and/or the content of octadecyl group. In the case of the copolymers, the melting point of the side chain further decreased because the crystallization of the side chain introduced seemed to be obstructed by the rigidity of the main chain [9]. Thus, the thermal behavior of the poly(DRF) bearing an *n*-alkyl side chain was utterly different from that of poly(DiPF) and poly(DtBF); poly(DiPF) and poly(DtBF) do not show any transition except for the motion of the ester groups and not melt below its decomposition temperature [5,12].

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