Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Otsu, Takayuki , Yasuhara, Takashi and Matsumoto, Akikazu(1988) 'Synthesis, Characterization, and Application of Poly[Substituted Methylene]S', Journal of Macromolecular Science, Part A, 25: 5, 537 — 554

To link to this Article: DOI: 10.1080/00222338808053383

URL: http://dx.doi.org/10.1080/00222338808053383

J. MACROMOL. SCI.–CHEM., A25(5-7), pp. 537-554 (1988)

SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF POLY(SUBSTITUTED METHYLENE)S

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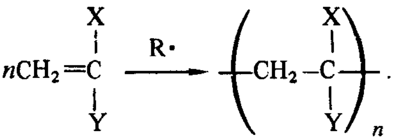
ABSTRACT

Radical polymerization of fumaric acid derivatives, such as dialkyl fumarates, gave polymers consisting of a less- or nonflexible substituted polymethylene structure. The yield and molecular weight of the polymers produced increased as the bulkiness of the ester substituents increased. For example, when di-*t*-butyl fumarate was polymerized in bulk with azocyclohexanecarbonitrile (20 mmol/L) at 80°C for 6 h, polymer with $\bar{M}_n$ of more than 100 000 was produced in more than 80% yield. The polymers obtained were colorless powders and did not melt before degradation at ~250°C, but they were soluble in such organic solvents as benzene, carbon tetrachloride, tetrahydrofuran, and dioxane. A transparent brittle film or fiber was obtained from toluene solution. Some properties and possibilities for application of these polymers are described and discussed.

INTRODUCTION

A number of monosubstituted ethylenes (X = H, Y = R) and 1,1-disubstituted ethylenes (X, Y = R) homopolymerize in the presence of radical initiator to give high molecular weight polymers consisting of a substituted polyethylene structure which has a methylene group in the recurring unit [1-3]:

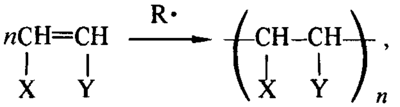


$$n\mathrm{CH_2{=}\overset{\displaystyle X}{\underset{\displaystyle Y}{C}}} \xrightarrow{\mathrm{R\cdot}} \left(\mathrm{CH_2{-}\overset{\displaystyle X}{\underset{\displaystyle Y}{C}}}\right)_n .$$

(1)

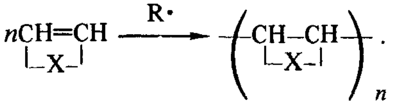
In these polymerizations the relationship between monomer structure and polymerization reactivity has been studied in detail on the basis of polar, resonance, and steric effects of the substituents, as well as the polymer structure-physical property relationship. Since the existence of such a methylene group makes these polymers flexible and processable, a number of plastic materials have been produced industrially.

On the other hand, it has been accepted that *cis* or *trans* and cyclic 1,2-disubstituted ethylenes, except for a few exceptions, which will be shown later, do not generally homopolymerize owing to the increased steric effect of the substituents [1-4]. However, if these ethylenes are homopolymerized, polymers with a substituted polymethylene structure will be produced, i.e., the polymer formation from these ethylenes is expressed by the following equations:



$$n\mathrm{\underset{\displaystyle X}{CH}{=}\underset{\displaystyle Y}{CH}} \xrightarrow{\mathrm{R\cdot}} \left(\mathrm{\underset{\displaystyle X}{CH}{-}\underset{\displaystyle Y}{CH}}\right)_n ,$$

(2)

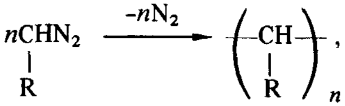


$$n\mathrm{\underbrace{CH{=}CH}_{X}} \xrightarrow{\mathrm{R\cdot}} \left(\mathrm{\underbrace{CH{-}CH}_{X}}\right)_n .$$

(3)

These polymers may be distinguished between polymethylenes with substituents independent from each other and those bearing a cyclized substituent, respectively. Such polymethylenes might be expected to reveal new properties different from those of polyethylenes, because the flexibility of the former decreases more than that of the latter.

As a main route for synthesizing such polymethylenes, the polymerization of diazoalkanes has been investigated by many workers [5-7]:



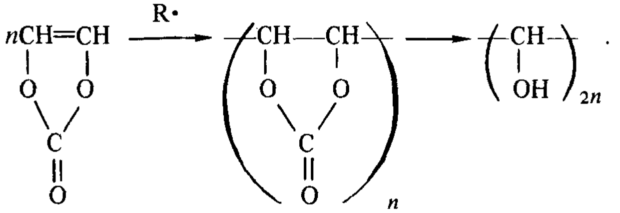
$$n\mathrm{\underset{\displaystyle R}{CH}N_2} \xrightarrow{-n\mathrm{N_2}} \left(\mathrm{\underset{\displaystyle R}{CH}}\right)_n ,$$

(4)

in which R is hydrogen or an alkyl group such as methyl or phenyl. The polymerization of diazomethane with boron trifluoride resulted in high molecular weight crystalline polymethylene [5-7], which was used as a model polymer for unbranched linear polyethylene until the discovery of high-density polyethylene by Ziegler [8] in 1953. The other diazoalkanes, however, gave only low molecular weight substituted polymethylenes [7, 9-12].

The cationic polymerization of some isonitriles [13] and the oxidative coupling polymerization of some disubstituted methanes [14] have also been reported to be synthetic routes to polymethylene derivatives, but their yield, molecular weight, and structure regularity were low.

As described above, a few cyclic 1,2-disubstituted ethylenes, such as vinylene carbonate [15-17], maleic anhydride [18], and maleimides [19-22], have been known to be homopolymerized. For example, radical polymerization of vinylene carbonate leading to a high molecular weight polymer, which is hydrolyzed to poly(hydroxymethylene), was found by Newman and Addor [15] in 1953, and subsequently studied by many workers [16, 17]:

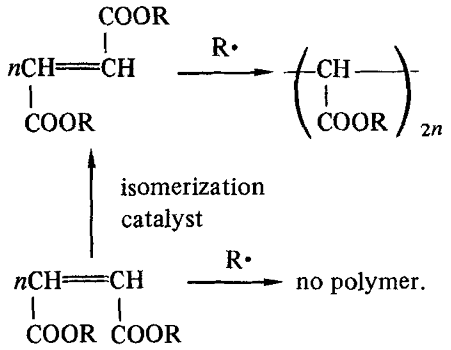


(5)

The poly(vinylene carbonate) and poly(hydroxymethylene) thus obtained did not melt before degradation, and the former was soluble only in acetone, dimethylformamide, and dimethylsulfoxide, but the latter was insoluble in any solvents including water [17], i.e., different from poly(vinyl alcohol).

The facile cationic polymerization of some linear 1,2-disubstituted ethylenes has been shown by Higashimura and coworkers [23]. Recently, they reported on the living cationic polymerization of *cis-* and *trans-*propenyl ethers with the HI/I_2 catalyst system [24]. In 1974, Nagasawa and coworkers [25] also found that *t*-butyl crotonate was polymerized with 2-methylbutyllithium to give a high molecular weight and semiflexible polymer with a narrow molecular weight distribution [25-27].

Radical high polymerization of linear 1,2-disubstituted ethylenes was reported by Bengough and coworkers [28] for diethyl fumarate in 1975. At almost the same time, we found that various dialkyl fumarates (DRF) [29-38] and dialkyl maleates (DRM) [39-43] were homopolymerized with radical initiator in the absence and presence of morpholine, respectively, as an isomerization catalyst from maleate to fumarate:



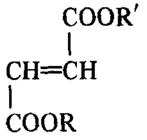
$$n\underset{\text{COOR}}{\text{CH}}=\overset{\text{COOR}}{\text{CH}} \xrightarrow{\text{R}\cdot} \left(\underset{\text{COOR}}{\text{CH}}\right)_{2n}$$

$$\uparrow \text{ isomerization catalyst}$$

$$n\underset{\text{COOR}}{\text{CH}}=\underset{\text{COOR}}{\text{CH}} \xrightarrow{\text{R}\cdot} \text{no polymer.} \qquad (6)$$

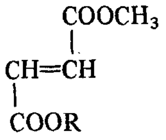
The polymers obtained from both fumarates and maleates were confirmed to consist of an identical poly(alkoxycarbonylmethylene) structure, and we proposed calling these polymerizations of maleates "monomer-isomerization radical polymerization" [39-43], in analogy to the monomer-isomerization polymerization of internal olefins with Ziegler-Natta catalysts [44, 45].

To clarify further the chemistry of these polymethylenes, the polymerization reactivities of some fumaric derivatives, DRF, methyl alkyl fumarates (MRF), alkyl *N,N*-diethylfumaramates (RFA), and *N,N,N′,N′*-tetraalkylfumaramides (TRFAm), were evaluated.



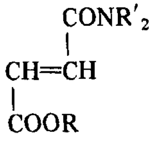
$\underset{\text{COOR}}{\text{CH}}=\overset{\text{COOR}'}{\text{CH}}$

(DRF)



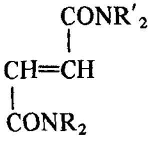
$\underset{\text{COOR}}{\text{CH}}=\overset{\text{COOCH}_3}{\text{CH}}$

(MRF)



$\underset{\text{COOR}}{\text{CH}}=\overset{\text{CONR}'_2}{\text{CH}}$

(RFA)



$\underset{\text{CONR}_2}{\text{CH}}=\overset{\text{CONR}'_2}{\text{CH}}$

(TRFAm)

Moreover, the characterization and application of the resulting polymers with bulky ester substituents were investigated. The results obtained are described in this paper.

EXPERIMENTAL

The DRF, MRF, RFA, and TRFAm used were prepared by fumaryl chloride with the respective alcohols or dialkylamines according to the methods reported in the literature, and purified by distillation or recrystallization.

Polymerizations were carried out in sealed tubes with shaking in a thermostat maintained at a given temperature. 2,2′-Azobisisobutyronitrile (AIBN) and 1,1′-azobiscyclohexanecarbonitrile (ACN) were used as initiators. After polymerization for an appropriate time, the polymerization mixture was poured into a large amount of precipitant to isolate the polymer, which then was purified by the usual reprecipitation method.

Intrinsic viscosities, $[\eta]$, were measured in benzene at 30°C. Number-average molecular weights, $\bar{M}_n$, were determined by membrane osmometry and GPC measurement. The structure of the polymers was revealed by IR and NMR spectroscopy. Thermal properties were determined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and pyrolysis gas chromatography (PGC) measurements.

RESULTS AND DISCUSSION

Polymerization Reactivities of Fumaric Acid Derivatives

DRF's and MRF's, β-alkoxycarbonylacrylic esters, did not give any polymer in the absence of radical initiator and in the presence of anionic initiators such as *n*-butyllithium. With radical initiators, however, the polymerizations were easily induced to give polymers consisting of a substituted polymethylene structure [35, 36]. Concentrations of the initiator (~10 times more) and the monomer (without solvent) higher than those for ordinary radical polymerization are necessary to achieve high polymerization because of the low reactivity of DRF's due to the increased steric effect of the substituent.

The results of radical polymerization of various DRF's and MRF's with AIBN or ACN in bulk are summarized in Table 1. From this table the polymerization reactivities, yield, and $[\eta]$ of the polymers were observed to be largely dependent on the structure of the ester substituents. The reactivities of DRF's with primary ester groups were low, and they did not change or decreased slightly with increasing length of the ester alkyl groups. However, they increased greatly in secondary and tertiary alkyl esters, i.e.,

TABLE 1. Radical Polymerization of DRF and MRF in Bulk[a]

Fumarate	R	R′	Temperature, °C	Time, h	Yield, %	$[\eta]$,[b] dL/g
DMF	Me	Me	90[c]	4	10.5	0.05
DEF	Et	Et	90[c]	4	33.4	0.10
DEF	Et	Et	60	10	10.0	0.20 (1.5)
DnPF	*n*-Pr	*n*-Pr	60	10	5.8	0.13
DiPF	*i*-Pr	*i*-Pr	60	10	29.1	0.86 (11.0)
DnBF	*n*-Bu	*n*-Bu	60	10	6.4	0.15
DiBF	*i*-Bu	*i*-Bu	60	10	5.4	0.12
DsBF	*s*-Bu	*s*-Bu	60	12	16.4	0.41 (6.9)
DtBF	*t*-Bu	*t*-Bu	60[d]	10	38.4	0.78
DtBF	*t*-Bu	*t*-Bu	80[e]	6	84.6	0.63 (10.0)
DtAF	*t*-Am	*t*-Am	60	10.6	3.2	0.21
DCHF	*c*-Hex	*c*-Hex	60	10	59.5	0.76 (11.2)
DEHF	2-EtHex	2-EtHex	60	10	7.1	0.08

MEF	Me	Et	60	10	4.8	0.10
MnPF	Me	*n*-Pr	60	10	4.3	0.10
MiPF	Me	*i*-Pr	60	10	10.4	0.21
MnBF	Me	*n*-Bu	60	10	4.0	0.08
MiBF	Me	*i*-Bu	60	10	2.5	0.08
MsBF	Me	*s*-Bu	60	10	7.8	0.16
MtBF	Me	*t*-Bu	60	10	23.5	0.45
MtAF	Me	*t*-Am	60	10	13.2	0.35
MPhF	Me	Ph	80[e]	10	0	–
MPhF	Me	Ph	130[f]	23	23.0	0.03
mMF	Me	H	80[c]	10	0	–
mMF	Me	H	130[g]	23	68.0	0.04

[a] Polymerized with AIBN (0.02 mol/L).

[b] In benzene at 30°C. Values in parentheses show $\bar{M}_n \times 10^{-4}$ determined by GPC.

[c] With ACN (0.02 mol/L).

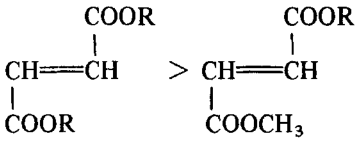
[d] In benzene; [DtBF] = 2.2 mol/L.

[e] With ACN (0.03 mol/L).

[f] Polymerized MPhF (5.4 g) in toluene (1.0 mL) with di-*t*-butyl peroxide (0.1 mL).

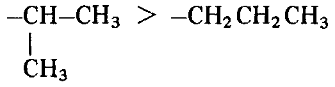
[g] Polymerized mMF (5.4 g) in toluene (1.0 mL) with di-*t*-butyl peroxide (0.1 mL).

the polymerization reactivities of DRF's and MRF's increase with an increase in the bulkiness of their ester substituents in the following order:

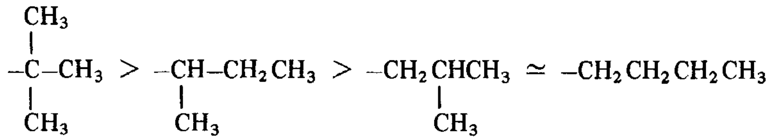


$$\underset{\text{COOR}}{\text{CH}}{=}\overset{\text{COOR}}{\text{CH}} > \underset{\text{COOCH}_3}{\text{CH}}{=}\overset{\text{COOR}}{\text{CH}}$$

Effect of R:



$$-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 > -\text{CH}_2\text{CH}_2\text{CH}_3$$



$$-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3 > -\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_3 > -\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_3 \simeq -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

These reactivity orders are the same as those of increasing steric effect of the ester substituents, which do not agree with the well-established conclusion in organic chemistry that reactivities decrease when the steric effect of the substituents increases.

However, the observed results may be understood as the characteristics of a radical polymerization which proceeds via a chain reaction consisting of four elementary steps. That is, because the polymer chain with bulky substituents becomes more rigid, it seems that bimolecular termination between such rigid propagating radicals having a bulky group was occurring less frequently, relative to the propagation reaction, thus giving higher molecular weights and faster polymerization rates.

DtAF and MtAF, which have more bulky substituents than DtBF and MtBF, respectively, showed low reactivities, probably indicating that the bulkiness of the *t*-amyloxycarbonyl substituents was too large to exhibit high ploymerization rates. DRF and MRF with phenyl and monomethyl ester substituents also hardly homopolymerized.

It is interesting to compare the results of Table 1 with those of the other maleic and fumaric derivatives. As stated before, maleic esters could undergo monomer-isomerization radical polymerization in the presence of both AIBN initiator and morpholine (as an isomerization catalyst) to give poly(alkoxycarbonylmethylene)s. In these cases the polymerization reactivities of the

TABLE 2. Radical Polymerization of RFA and TRFAm with ACN at 80°C[a]

Monomer	R	R′	Time, h	Yield, %	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$
RFA	Me	Et	50	10.3	11[c]	1.3
RFA	*i*-Pr	Et	30	12.8	7[d]	1.3
TRFAm	Et	Et	10[e]	30.4	12	1.7
TRFAm	*n*-Pr	*n*-Pr	12[e]	25.3	15	1.8
DRF	*i*- Pr	*i*-Pr	10[f]	29.1	110	2.0

[a] Polymerization conditions: [ACN] = 20 mmol/L in bulk.

[b] Determined by GPC.

[c] $\bar{M}_n$ = 23 000 by membrane osmometry.

[d] $\bar{M}_n$ = 13 000 by membrane osmometry.

[e] The monomer (5 mmol) was polymerized with ACN (0.05 mmol) in benzene (5 mL).

[f] Polymerized with AIBN at 60°C.

maleates were also found to be correlated with those of DRF's isomerized [34] and with their isomerization rates [43].

Table 2 shows the results of radical homopolymerization of some RFA and TRFAm. These fumaric derivatives were also homopolymerized in the order TRFAm > RFA, but the $\bar{M}_n$ of the polymers obtained was not as high (10 000 to 23 000) as with that from DiPF. However, the other derivatives containing carboxyl and unsubstituted amide groups did not polymerize, because these compounds were solid under the polymerization conditions.

Polymerization Characteristics of DRF's with Bulky Ester Substituents

Time-conversion relations for radical polymerizations of DCHF in bulk and of DtBF in benzene are shown in Figs. 1 and 2, respectively. These polymerizations proceeded easily without an induction period, and the $[\eta]$ of the polymers produced did not change, irrespective of the reaction time, like ordinary radical polymerization of vinyl monomers.

By plotting the initial rates of polymerization (R_p) determined with the reciprocal of the absolute polymerization temperatures, the apparent activation energies for overall polymerizations of DCHF and DtBF were calculated as 85.8 and 83.4 KJ/mol, respectively. These values were similar to those re-

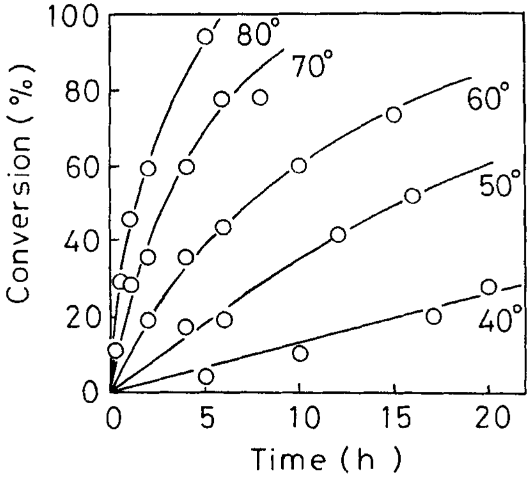


FIG. 1. Time-conversion relations for bulk polymerization of DCHF with AIBN at 40-80°C; [AIBN] = 20 mmol/L.

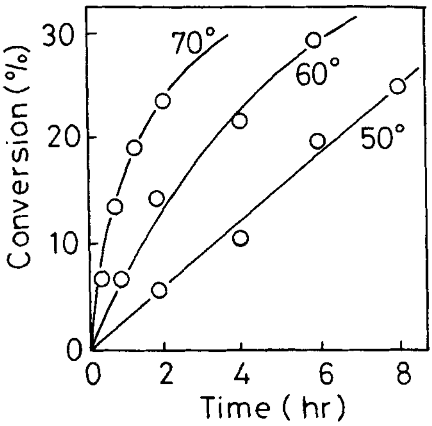


FIG. 2. Time-conversion relations for the polymerization of DtBF with AIBN in benzene at 50-70°C; [DtBF] = 2.2 mol/L, [AIBN] = 20 mmol/L.

ported for methyl methacrylate (85.0 kJ/mol) and styrene (94.5 KJ/mol), indicating that these polymerizations proceeded by an ordinary free-radical mechanism.

The dependence of R_p on the monomer and initiator concentrations is noted. The observed orders with respect to the monomer concentration were higher (1.6, 2.4, and 2.5 for DEF, DiPF, and DtBF, respectively) than those (~1.0) for ordinary vinyl monomers, and they were in agreement with the increasing order of bulkiness of the substituents. A similar high order (2.3) was found for radical polymerization of vinylene carbonate [46]. As will be described later, it seems to come from the low reactivity of DRF's as a 1,2-disubstituted ethylene.

The orders with respect to the initiator concentration were also found to change with the ester substituents of DRF's in bulk polymerizations, i.e., 0.50, 0.59, and 0.38 for DEF, DiPF, and DtBF, respectively. Moreover, these orders changed when the polymerizations were carried out in benzene solution (~50% monomer), i.e., 0.37, 0.30, and 0.28 for DEF, DiPF, and DtBF, respectively, indicating that primary radical termination becomes important in comparison with mutual termination when the bulkiness of the substituents increases and the monomer concentration decreases.

The absolute rate constants k_p and k_t for the polymerization of DEF at 30°C were determined by a rotating sector method to be 0.015 and 164 L/(mol·s), respectively. These values were much smaller compared to those for styrene and ethyl acrylate polymerizations ($k_p = 106$ and 1300, and $k_t = 7.2 \times 10^7$ and 2.7×10^7 L/(mol·s), respectively), indicating that the steric effects of β-substituents in DEF monomer and its radical play a very important role in these reactions. However, the ratio of k_p to $k_t^{0.5}$ was similar to that for ordinary vinyl monomers, thus giving faster polymerization rates and higher molecular weights, the same as ordinary radical polymerization.

However, the values of k_p and k_t for DRF's with more bulky ester substituents, such as DiPF, were not determined by the rotating sector method, because the lifetime of their propagating radical was too long. This may mean that the concentration of the propagating radical is quite high, and hence, the values of k_p and k_t are very small. In fact, the ESR spectra due to the propagating poly(DRF) radicals were found to be easily detected at room temperature, as shown in Fig. 3. The observed ESR spectra decayed at a very slow rate through mutual termination. The rate of decay was also found to depend on the structure of the ester substituents, i.e., when their bulkiness increased, the rate of decay decreased.

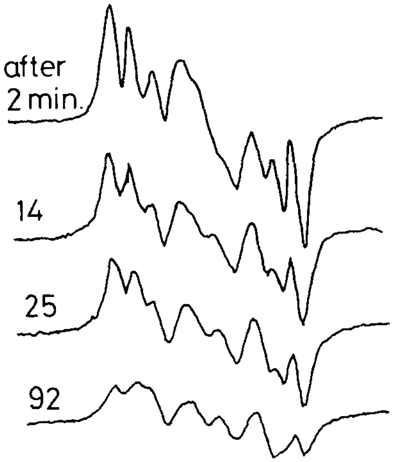


FIG. 3. Decay of the ESR spectrum of poly(DiPF) propagating radical after interception of UV irradiation at room temperature.

Characterization of Poly(Alkoxycarbonylmethylene)s

The poly(DRF)'s thus obtained were colorless powders. Transparent beads were also obtained from suspension polymerization of DiPF. These polymers gave elementary analysis data in good agreement with those calculated for poly(DRF)'s. In addition, ^{1}H- and ^{13}C-NMR spectra showed that these polymers possess a polymethylene structure [35, 36].

Figure 4 shows the molecular model (similar to the CPK models) of poly(DiPF), i.e., poly(isopropoxycarbonylmethylene). It is clear that this polymer is less flexible and more rigid than ordinary vinyl polymers. The calculated diameter and the end-to-end distance of this rod polymer were about 1.4 and 120 nm, respectively, for $\bar{M}_n$ equal to 100 000. In general, the rigidity of poly(DRF)'s might be expected to increase with increasing bulkiness of the substituents.

An x-ray diffraction photograph of the undrawn poly(DiPF) film is shown in Fig. 5, from which the Bragg spacings were determined to be 1.04(s) and 0.44(w) nm. Similar results were also reported by Yamada, Takayanagi, and Murata [47]. From Fig. 5, the crystallinity of this polymer was determined to be about 60%, but its stereoregularity is uncertain at the present time.

To elucidate further the rigidity of these polymers, the relationship be-

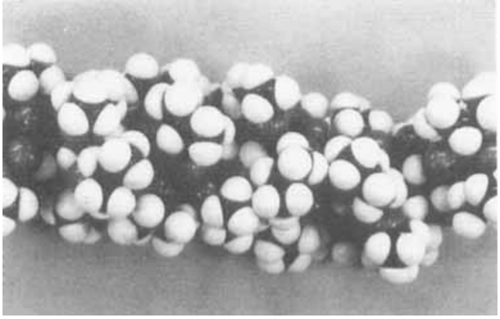


FIG. 4. Molecular model for poly(DiPF).

tween $\bar{M}_n$ and $[\eta]$ of poly(DiPF) was determined at 30°C. The values of K and α in $[\eta] = K \cdot \bar{M}_n{}^a$ were found to be [36] $K = 7.67 \times 10^{-6}$, $\alpha = 1.0$ [unfractionated poly(DiPF) in toluene] and $K = 9.65 \times 10^{-6}$, $\alpha = 0.98$ [fractionated poly(DiPF) in benzene]. The observed α-value, which was the largest value among vinyl polymers prepared by polymerization and close to those

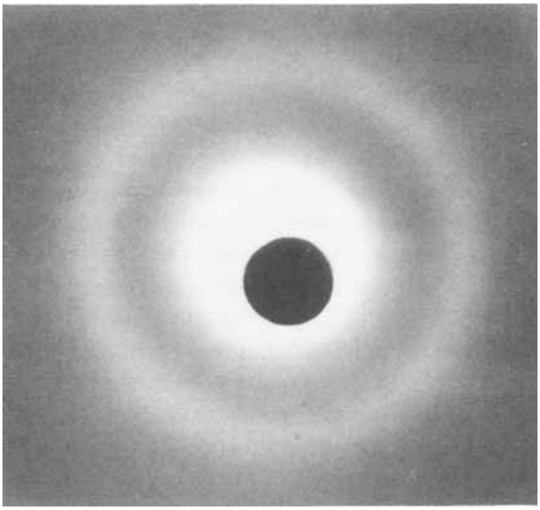


FIG. 5. Wide-angle x-ray diffraction photograph of poly(DiPF).

TABLE 3. Physical Properties of Poly(DiPF)

Specific gravity: 1.12 g/cm^3

Refractive index: 1.460

Solubility: Soluble in benzene, carbon tetrachloride, tetrahydrofuran, and dioxane

Weathering and UV stability: Excellent

Hydrolysis: Very difficult

Thermal stability: T_{init} = 223°C, T_{max} = 300°C, residue at 500°C = 11.9%

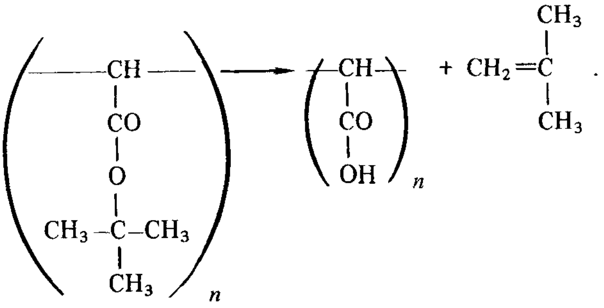
T_g and T_m (DSC): Do not show below decomposition temperature

of cellulose derivatives [48], strongly indicates that poly(DiPF) is a less flexible, rodlike polymer.

Some physical properties of poly(DiPF) are summarized in Table 3. Since poly(DRF)s are also derivatives of poly(acrylic esters), i.e., poly(alkyl β-alkoxycarbonylacrylate), excellent transparency and UV stability, wheather resistance, and hydrolysis are essentially the same as those of poly(acrylic esters) including poly(methyl methacrylate). However, the thermal properties are different. From DSC measurement, poly(DiPF) does not show a clear glass transition temperature (T_g) below its degradation temperature. Takayanagi et al. [47] reported that a small absorption at 97°C, which corresponds to the motion of ester groups, was observed in the temperature dependence of the storage and loss modulus of the poly(DiPF) film.

Thermal degradation of poly(DRF)'s with primary and secondary ester groups was performed by one-step reaction, and initial and maximum degradation temperatures, T_{init} and T_{max}, were determined as follows: T_{init} = 240-250°C, T_{max} = 380-390°C for poly(DRF)'s with primary ester groups like poly(DEF), and T_{init} = 230-250°C, T_{max} = 290-300°C for poly(DRF)'s with secondary ester groups including poly(DiPF). From pyrolysis gas chromatographic determination at 400°C in nitrogen atmosphere, the main degradation products were confirmed to be the respective alcohols and DRF monomers, and the ratios of alcohol to monomer were 9.5 and 32.0 for poly(DEF) and poly(DiPF), respectively.

However, thermal degradation of poly(DRF)'s having tertiary ester groups, like poly(DtBF), proceeded by a two-step reaction, i.e., the first decomposition occurred at 190°C and the second decomposition started from 290°C (T_{init}). The thermogram of poly(DtBF) at 200°C showed one peak which was confirmed to be isobutene. Therefore, it was clear that the first decomposition proceeded according to



$$\left(\begin{array}{c}-CH-\\ |\\ CO\\ |\\ O\\ |\\ CH_3-C-CH_3\\ |\\ CH_3\end{array}\right)_n \longrightarrow \left(\begin{array}{c}-CH-\\ |\\ CO\\ |\\ OH\end{array}\right)_n + \begin{array}{c}CH_3\\ |\\ CH_2{=}C\\ |\\ CH_3\end{array} . \qquad (7)$$

The formation of poly(fumaric acid), i.e., poly(hydroxycarbonylmethylene), was confirmed by IR and NMR. Similar reactions were observed to occur for the copolymers of styrene with DtBF. Therefore, these thermal reactions are a novel route for the synthesis of high molecular weight poly(FA) and the introduction of an acid group into polymers.

Application of Poly(Alkoxycarbonylmethylene)s

As stated above, the polymerization reactivities of DRF's and the physical properties of the resulting poly(DRF)'s widely changed with their ester substituents. Moreover, copolymerizations with various vinyl monomers might also give copolymers with a modified property.

In general, poly(DRF)'s with bulky substituents like poly(DiPF) and poly(DtBF) do not melt. However, since these polymers were soluble in some organic solvents, a transparent film, sheet, or fiber was obtained from their toluene solution. Moreover, transparent molding products, which are useful for optical materials, were also prepared by cast polymerization of DRF's.

The poly(DRF)'s showed good compatibility with acrylic and methacrylic polymers. Therefore, this might be expected to apply to modification of these polymers in order to improve thermal and mechanical properties.

High molecular weight rodlike polyacetylenes with bulky substituents were shown by Higashimura et al. [49] to serve as excellent oxygen-enrichment membranes. Similarly, the polymer membranes of poly(DRF)'s with bulky substituents, such as poly(DCHF), were found to be highly permeable to oxygen compared to nitrogen [50]. Therefore, these are expected to be applicable to a new oxygen-enrichment membrane.

ACKNOWLEDGMENT

The authors gratefully acknowledge a supply of DRF monomers by Tsukuba Laboratory, Nippon Oil & Fats Co., Ltd.

REFERENCES

[1] T. Otsu, *Prog. Polym. Sci. Jpn., 1,* 1-68 (1971).

[2] T. Otsu, *Radical Polymerization (I) Elementary Reaction Mechanism,* Kagaku Dojin, Kyoto, 1971.

[3] T. Yonezawa and T. Otsu, *Radical Polymerization (II) Copolymerization and Monomer Reactivities,* Kagaku Dojin, Kyoto, 1977.

[4] T. Alfrey Jr., J. J. Bohrer, and H. Mark, *Copolymerization,* Interscience, New York, 1951.

[5] H. Meerwein, *Angew. Chem., 60,* 78 (1948).

[6] S. W. Kantor and R. C. Osthoff, *J. Am. Chem. Soc., 75,* 931 (1953).

[7] G. D. Buckley, L. H. Cross, and N. H. Ray, *J. Chem. Soc.,* p. 2714 (1950).

[8] K. Ziegler, E. Holzkampf, H. Breil, and H. Martin, *Angew. Chem., 67,* 541 (1955).

[9] J. Feltzin, A. J. Restaine, and R. B. Mesrobian, *J. Am. Chem. Soc., 77,* 206 (1955).

[10] C. E. H. Bawn and A. Ledwith, *Chem. Ind.,* p. 1180 (1957).

[11] C. E. H. Bawn, A. Ledwith, and p. Mattheis, *J. Polym. Sci., 33,* 21 (1958).

[12] A. G. Nasini, L. Trossarelli, and G. Saini, *Makromol. Chem., 44/46,* 550 (1961).

[13] I. Yamamoto, T. Takizawa, and N. Hagiwara, *Nippon Kagaku Kaishi, 87,* 1355 (1966); *Ibid., 89,* 898 (1968).

[14] V. V. Korshak, S. L. Sosin, and V. P. Alekseeva, *J. Polym. Sci., 52,* 213 (1961); *Vysokomol. Soedin., 3,* 1116 (1961); *Ibid., 5,* 499 (1963).

[15] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc., 75,* 1263 (1953).

[16] K. Hayashi and G. Smets, *J. Polym. Sci., 27,* 626 (1958).

[17] N. D. Field and J. R. Schaefgan, *Ibid., 58,* 533 (1962).

[18] N. G. Gaylord, *J. Macromol. Sci.-Rev. Macromol. Chem., C13,* 235 (1975).

[19] P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams, *J. Org. Chem., 26,* 15 (1961).

[20] R. M. Joshi, *Makromol. Chem., 62,* 140 (1963).

[21] R. C. P. Cubbon, *Polymer, 6,* 419 (1965).

[22] M. Yamada, I. Takase, and N. Koutou, *J. Polym. Sci., Part B, 6,* 883 (1968).

[23] T. Higashimura, *Cationic Polymerization,* Kagaku Dojin, Kyoto, 1971, pp. 227-243.

[24] T. Higashimura and M. Sawamoto, *Adv. Polym. Sci., 62,* 49 (1984); M. Sawamoto, K. Ebara, A. Tanizaki, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed., 24,* 2919 (1986).

[25] T. Kitano, T. Fujimoto, and M. Nagasawa, *Macromolecules, 7,* 719 (1974); T. Kitano, M. Mitsumura, T. Fujimoto, and M. Nagasawa, *Ibid., 8,* 382 (1975).

[26] I. Noda, T. Imai, T. Kitano, and M. Nagasawa, *Ibid., 14,* 1303 (1981).

[27] I. Noda, Y. Yamamoto, T. Kitano, and M. Nagasawa, *Ibid., 14,* 1306 (1981).

[28] W. I. Bengough, G. B. Park, and R. A. Young, *Eur. Polym. J., 11,* 305 (1975).

[29] T. Otsu and T. Ishikawa, *Polym. Prepr. Jpn., 28,* 514 (1979).

[30] T. Otsu, O. Ito, N. Toyoda, and S. Mori, *Makromol. Chem., Rapid Commun., 2,* 725 (1981).

[31] T. Otsu, O. Ito, N. Toyoda, and S. Mori, *Mem. Fac. Eng., Osaka City Univ., 22,* 129 (1981).

[32] T. Otsu, N. Toyoda, O. Ito, and S. Mori, *Ibid., 23,* 79 (1982).

[33] N. Toyoda and T. Otsu, *J. Macromol. Sci.–Chem., A19,* 1011 (1983).

[34] T. Otsu and N. Toyoda, *Polym. Bull., 11,* 453 (1984).

[35] T. Otsu. T. Yasuhara, K. Shiraishi, and S. Mori, *Ibid., 12,* 449 (1984).

[36] T. Otsu, H. Minai, N. Toyoda, and T. Yasuhara, *Makromol. Chem., Suppl., 12,* 133 (1985).

[37] T. Otsu, A. Matsumoto, and K. Fukushima, *J. Chem. Soc., Chem. Commun.,* p. 1766 (1985).

[38] T. Otsu, K. Shiraishi, A. Matsumoto, T. Yasuhara, N. Amaya, and S. Mori, *Polym. Commun., 26,* 367 (1985).

[39] T. Otsu and N. Toyoda, *Makromol. Chem., Rapid Commun., 2,* 79 (1981).

[40] T. Otsu, O. Ito, and N. Toyoda, *Ibid., 2,* 729 (1981).

[41] T. Otsu, O. Ito, and N. Toyoda, *J. Macromol. Sci.–Chem., A19,* 27 (1983).

[42] N. Toyoda, M. Yoshida, and T. Otsu, *Polym. J., 15,* 255 (1983).

[43] T. Otsu and K. Shiraishi, *Macromolecules, 18,* 1795 (1985).

[44] J. P. Kennedy and T. Otsu, *Adv. Polym. Sci., 7,* 369 (1970).

[45] K. Endo and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed., 24,* 1605, 1615, 1633 (1986).

[46] T. Otsu and N. Murata, Unpublished Results.
[47] K. Yamada, M. Takayanagi, and Y. Murata, *Rep. Prog. Polym. Phys. Jpn.*, *27*, 321 (1984).
[48] J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, Chap. IV.
[49] T. Higashimura, T. Masuda, and M. Okada, *Polym. Bull.*, *10*, 114 (1983).
[50] H. Ikebe, Y. Murata, and T. Otsu, *Polym. Prepr. Jpn.*, *34*, 420 (1985).