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Preparation and properties of *disyndiotactic* poly(alkyl crotonate)s

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Abstract

Ethyl, *n*-propyl, *iso*-propyl and *n*-butyl crotonates were polymerized by group transfer polymerization (GTP) using ketene trialkylsilyl acetals as initiators in the presence of mercury (II) iodide as catalyst and iodotriethylsilane as co-catalyst. Predominantly *disyndiotactic* polymers with number-average molecular weights ranging from 56,000 to 90,000 were obtained almost quantitatively. Thermal and mechanical properties of poly(alkyl crotonate)s, such as glass transition temperature (T_g), refractive index, transmissivity, Izod impact strength, Young's modulus, hardness, tensile strength, tensile elongation at break, gas permeability coefficient and density were measured. All the polycrotonates have 65–90 °C higher T_g than the corresponding polymethacrylates.

Keywords: Group transfer polymerization; Ditacticity; Stereospecific polymerization

1. Introduction

Despite the similarity in their chemical structures, crotonate and methacrylate have quite different reactivity in polymerization reactions. Reluctance to homopolymerization by free radical mechanism is a commonly observed feature of crotonates [1,2]. Typical anionic initiators such as alkyllithiums and Grignard reagents are effective for the polymerization of branched alkyl crotonates (i.e. *t*-butyl [1–8,13], isopropyl [2,3,9], *sec*-butyl [2,9–11], *sec*-hexyl (1-methylpentyl) [2], *sec*-octyl (1-methylheptyl) [2], isobornyl [2], 1-phenylethyl [2], phenyl [2], neopentyl (2,2-dimethylpropyl) [2], cyclohexyl [2], *tert*-amyl (1,1-dimethylpropyl) [5], 1-adamantyl [5], 3,5-dimethyl-1-adamantyl [5], and triphenylmethyl [12,14] crotonates), but not for the polymerization of methyl and *n*-alkyl crotonates. The only compound that has been known to polymerize *n*-alkyl crotonate in a substantial yield is calcium tetraethylzincate; the polymerization of ethyl, *n*-propyl, and *n*-butyl crotonate with this complex in toluene at −78 °C for 96 h affords polymers in 22–29% yields [9].

In the previous papers [15,16], we reported the group transfer polymerization (GTP) of methyl crotonate (MeC) catalyzed by HgI_2 and iodotrialkylsilane (R_3SiI) (Scheme 1; $R{=}CH_3$). This GTP is not only living in the temperature range from −40 to 0 °C, but also stereospecific to give *disyndiotactic* poly(methyl crotonate) (PMeC) (Scheme 2) with a narrow molecular weight distribution (MWD).

The physical properties of injection-molded specimens of polymers of *iso*-propyl, *sec*-butyl and cyclohexyl crotonates were examined in some detail [10]. The polymers exhibit a desirable combination of high service temperatures and good impact resistance for a vinyl homopolymer but were extremely difficult to mold.

Tsuruta et al. reported softening points of several poly(alkyl crotonate)s, which were higher than 260 °C (alkyl = methyl: > 320 °C, ethyl: 300 °C, *n*-propyl: 290 °C, *iso*-propyl: 288 °C, *n*-butyl: 280 °C, *sec*-butyl: 260 °C) [9]. Matsumoto et al. reported thermal degradation temperatures of several polycrotonates; the maximum decomposition temperatures of poly(1-adamantyl crotonate), poly(3,5-dimethyl-1-adamantyl crotonate) and poly(methyl crotonate) were 428, 418 and 400 °C, respectively [5]. These data indicate that polycrotonates have excellent thermal stability.

As mentioned above, only several attempts have so far been made at polymerization and properties of the polycrotonates. The present paper reports polymerization of various alkyl crotonates and several properties of polycrotonates including thermal and mechanical properties

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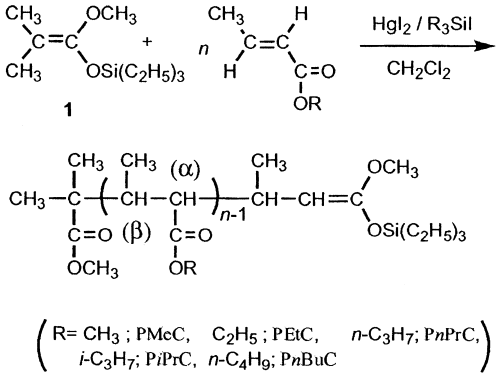
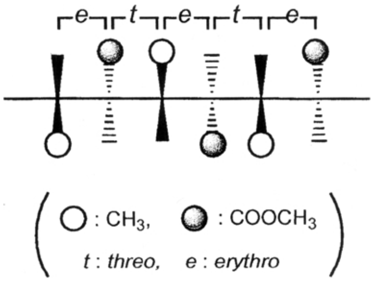


Scheme 1. GTP of alkyl crotonates.



Scheme 2. *Disyndiotactic* poly(methyl crotonate) [PMeC].

by GTP to obtain polycrotonates with well-defined structure [17].

2. Experimental

2.1. Materials

Ethyl crotonate (EtC) purchased from Nakalai tesque and methyl crotonate (MeC), *n*-butyl crotonate (*n*BuC) and *t*-butyl crotonate (*t*BuC) from TOKYO KASEI were purified by fractional distillation (bp 78.8–79.0 °C/100 Torr, bp 88.0–88.8 °C/31 Torr, bp 63.5–64.1 °C/31 Torr, respectively), dried over CaH_2, and then vacuum distilled just before use. All the monomers contained small amounts of isocrotonates as isomeric impurity. The chemical purity of EtC was >99.6% including ethyl isocrotonate (0.29%), that of *n*BuC was 99.2% including *n*-butyl isocrotonate (0.36%) and that of *t*BuC was 99.9% including *t*-butyl isocrotonate (0.03%) by GC. *n*-Propyl crotonate was prepared by transesterification of MeC in propan-1-ol [18]. *i*-Propyl crotonate was prepared by esterification from crotonic acid and propan-2-ol adding a small amounts of conc. H_2SO_4 [19]. PrC and *i*PrC were purified by fractional distillation (bp 100.1–101.1 °C/105 Torr, bp 82.4–82.9 °C/82 Torr, respectively). The chemical purity of *n*PrC was 99.8% with the isomer undetected, and that of *i*PrC was 99.8% including *iso*-propyl isocrotonate (0.14%).

1-Methoxy-1-(triethylsiloxy)-2-methyl-1-propene (**1**) used as initiator was prepared by a similar procedure described in the literature [20]. $(C_2H_5)_3SiI$ was prepared from $(C_2H_5)_3SiH$ and CH_3I in the presence of $PdCl_2$ according to the literature [21], and purified by fractional distillation (bp 71–72 °C/17 Torr, purity >99%).

Chemical purity of the above-mentioned reagents was determined by using a Hewellet Packard 6890 gas chromatograph equipped with an HP-5 fused-silica capillary column (0.32 mm × 30 m) and a built-in flame-ionization detector.

HgI_2 (99.9%) purchased from Wako Pure Chemical was dried in vacuo at room temperature for 20 min and used.

2.2. Polymerization and purification

Polymerization was initiated by adding the initiator in CH_2Cl_2 to a stirred mixture of monomer, HgI_2 and $(C_2H_5)_3SiI$ in CH_2Cl_2 under dry nitrogen atmosphere. After predetermined period of polymerization, a small amount of HCl/CH_3OH (ca. 1 M) was added to the mixture, and then CH_2Cl_2 was added to dissolve the resulting polymer. The solution was poured into a large amount of CH_3OH. The precipitated polymer was collected by filtration, and washed several times with CH_3OH and dried at 60 °C for 5 h.

When polycrotonates were precipitated into methanol twice, the ratio of remaining Hg to polymer became less than 0.01 mg kg^{-1}. The remaining Hg was measured by atomic absorption spectrometry with a Nippon Instruments Corporation MD-1.

2.3. Preparation of samples for various test of mechanical properties

2,2′-Methylenebis(4-ethyl-6-*tert*-butylphenol) and dioctadecyl 3,3′-thiodipropionate were added to polycrotonates as anti-oxidant with 0.25 wt% each for the polymers, and the mixtures were molded for measuring mechanical and thermal properties at 180–260 °C (P*n*PrC and P*n*BuC: 180 °C, P*i*PrC: 230 °C, PEtC: 260 °C).

2.4. Measurements

Number-average molecular weight ($\bar{M}_n$) was determined by ^{1}H NMR spectroscopic end-group analysis, where the relative intensities of the ester OCH or OCH_2 group and OCH_3 of end-group resonances (3.62 ppm) were used. The ^{1}H NMR spectra were measured in $CDCl_3$ at 55 °C on a Varian Unity-Inova 750 spectrometer. Size exclusion chromatography (SEC) was performed on a JASCO PU-980 chromatograph equipped with Polymer Laboratories SEC columns PLgel Mixed-D (7.5 mm × 300 × 2, maximum porosity 4×10^5) and a JASCO RI-930 detector using $CHCl_3$ as an eluent at 40 °C. Molecular weight was calibrated against standard PMMA samples (Shodex).

Intrinsic viscosities were measured in chloroform at 25.0 °C by using an Ubbelohde's viscometer.

T_g was determined by dynamic mechanical analysis

Table 1
Group transfer polymerization of crotonates with 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene (**1**) in the presence of HgI_2 and Et_3SiI in CH_2Cl_2

Crotonate		**1** (mmol)	Temp. (°C)	Time (h)	Yield (%)	$\bar{M}_n$			$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w$[b]	$[\eta]$[c] (dl g^{-1})
Ester	mol					Calcd[d]	NMR[e]	SEC[a]			
Et	1.00	2.50	−10	48	98	44,800	56,000	84,000	1.45	81,200	0.74
n-Pr	1.01	3.33	0	24	99	38,600	73,000	68,000	1.07	78,100	0.46
i-Pr[f]	1.00	2.50	0	96	100	51,400	71,000	74,000	1.07	76,000	0.54
n-Bu	0.82	2.45	−10	96	91	43,400	90,000	88,000	1.16	104,000	0.61

$[\text{Crotonate}]_0:[HgI_2]_0:[Et_3SiI]_0 = 1:0.0016:0.0075$; CH_2Cl_2, 200 ml.

[a] By size exclusion chromatography calibrated against standard PMMAs (eluent: $CHCl_3$).

[b] $\bar{M}_w$ estimated from $\bar{M}_n$ by NMR and $\bar{M}_w/\bar{M}_n$ by SEC.

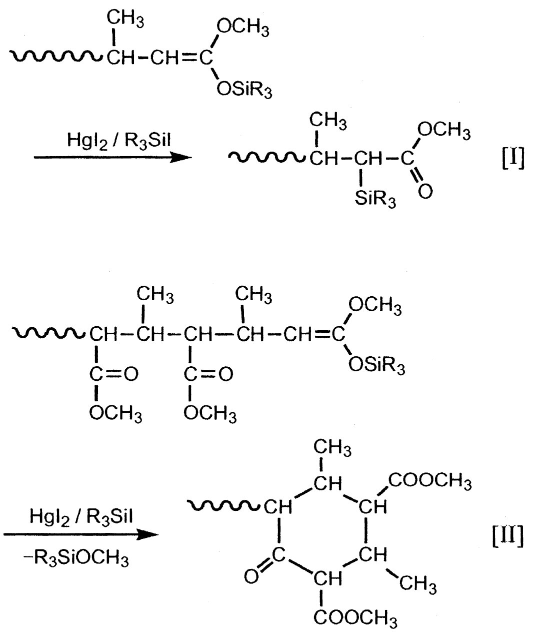
[c] At 25.0 °C in $CHCl_3$.

[d] Calculated from the yield and the feed ratio of monomer to initiator.

[e] By ^{1}H NMR end-group analysis.

[f] $[\text{Crotonate}]_0:[HgI_2]_0:[Et_3SiI]_0 = 1:0.0016:0.0048$; CH_2Cl_2, 400 ml.

(DMA) with a SEIKO DMS 6100 instrument in the temperature range of −140 to +200 °C at the temperature scanning rate of 2 °C min^{-1} and 1 Hz frequency. Thermogravimetry was performed on a SEIKO TG/DTA 6200 apparatus under nitrogen flow (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The degradation temperature (T_d) is defined as the temperature at which weight loss reaches 50% of the total weight loss. Gas permeability coefficients were measured with a TOYOSEIKI MT-C3 at 23 °C in nitrogen and oxygen. Tensile strength, Young's modulus and tensile elongation at break were measured with ORINTEC TENSILON at 23 °C. The Izod impact test was conducted at 23 °C by means of a cantilever beam machine. Hardness test was conducted according to ASTM D 2240 SHORE-D.



Scheme 3.

3. Results and discussion

3.1. Group transfer polymerization of crotonates

We have reported that the polymerization of MeC with 1-methoxy-1-(triethylsiloxy)-2-methyl-1-propene (**1**) (see Scheme 1) as an initiator in the presence of HgI_2 and $(C_2H_5)_3SiI$ in CH_2Cl_2, at a feed ratio MeC/**1**/HgI_2/$(C_2H_5)_3SiI$ of 10/0.2/0.016/0.0048, proceeds smoothly at −20 °C to give a polymer with narrow MWD in a quantitative yield [16]. To obtain higher molecular weight PMeC suitable for mechanical testing, a similar polymerization was conducted at MeC/**1** ratio of 200 under otherwise identical conditions. However, the yield at 24 h was only 23% and the longer polymerization time did not improve the yield. Moreover, $\bar{M}_w/\bar{M}_n$ value became a little broader (1.22). The reason might be attributed enhanced contribution of self-termination such as O-to-C silyl isomerization [I] and/or cyclization [II] (Scheme 3), which are not evident in the synthesis of relatively low molar mass PMeC.

Polymerizations of EtC, *n*PrC, *i*PrC and *n*BuC were conducted by using the same initiator system in CH_2Cl_2 at 0 or −10 °C. The results are shown in Table 1. Under the appropriate conditions indicated, all the monomers were polymerized smoothly to give polymers with $\bar{M}_n$'s ranging from 5×10^4 to 9×10^4 with fairy narrow MWD except for PEtC ($\bar{M}_w/\bar{M}_n = 1.45$). Under the conditions employed, *t*-BuC did not give any polymeric products.

Fig. 1 shows ^{1}H NMR spectra of several polycrotonates obtained with $HgI_2/(C_2H_5)_3SiI$ mediated GTP. The spectrum of PMeC (Fig. 1(a)) has been identified as *disyndiotactic* from the comparison with other ditactic PMeC's as well as with pure *disyndiotactic* oligomers whose structures were established by single-crystal X-ray analysis [16]. The characteristic β-CH_3 signals have been assigned as *etet* sequence as shown in the figure; *e* and *t* denote *erythro* and *threo*, respectively, (see Scheme 2).

Other polycrotonates also show similar β-CH_3 signal patterns, though some overlap signals due to side-chain

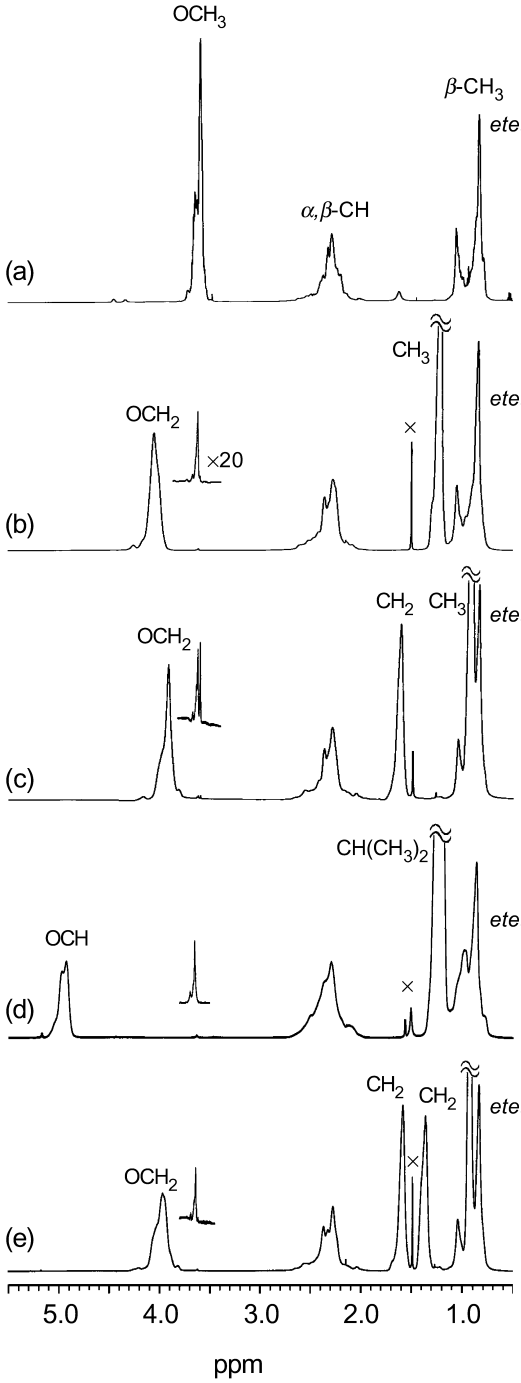


Fig. 1. ^{1}H NMR spectra of *disyndiotactic* polymers of methyl (a), ethyl (b), *i*-propyl (c), *n*-propyl (d), and *n*-butyl (e) crotonates (CDCl$_3$, 55 °C, 750 MHz), and in 'etet' denote and configurations of the neighboring substituents (CH$_3$ and COOR) (see Scheme 2).

ester group hinder the clear observation. Signals due to α- and β-CH protons are also sensitive to ditacticity. The similarity of α- and β-CH signals among these polycrotonates supports that all the polycrotonates obtained by this GTP are predominantly *disyndiotactic*.

Magnified signals at 3.6 ppm inserted in Fig. 1 are due to OCH$_3$ group at the initiating chain-end derived from **1**. As described in the experimental section, the signals are used effectively to estimate $\bar{M}_n$ values of the polymers as shown in Table 1. The M_n values thus obtained are in good agreement with those determined by SEC with PMMA calibration except for PEtC. Table 1 includes intrinsic viscosity data for the polymers measured in chloroform at 25.0 °C. While $\bar{M}_w$ values of the polymers are in the same order, the $[\eta]$ value for PEtC is exceedingly larger than the others. This implies the larger hydrodynamic volume of PEtC and explains the deviation of molecular weight determined by SEC from that determined by ^{1}H NMR end-group analysis.

3.2. Properties of polycrotonates

To estimate glass transition temperatures (Tg's) of the polycrotonates, differential scanning calorimetry (DSC) was examined in the temperature range of -50 to $+200$ °C at a heating rate of 10 °C min^{-1}. However, DSC showed no obvious T_g for the polycrotonates. Thus DMA measurement was conducted in the temperature range of -140 to $+200$ °C at a heating rate of 2 °C min^{-1} and 1 Hz frequency (Fig. 2). Maximum points of tan δ are regarded as T_g of the polycrotonates. Table 2 shows T_g and T_d of a series of poly(*n*-alkyl crotonate)s and polymethacrylates. PMeC did not show T_g below T_d of PMeC, so that molding of PMeC was very difficult. Other polycrotonates show T_g, which decreases with increasing number of carbons in the ester group. A similar tendency has already been known for polymethacrylates [22] The values of T_g's are about 65–90 °C higher than those for the respective polymethacrylates. T_d's of the polycrotonates are also higher than the respective polymethacrylates by 15–40 °C. The reason for the higher thermal property values may be ascribable to the main-chain stiffness of polycrotonates which have α- and β-substituents. Another important reason is that the polycrotonates have a high disyndiotacticity.

Table 3 summarized several mechanical properties of a series of poly(alkyl crotonate)s. As described above, PMeC

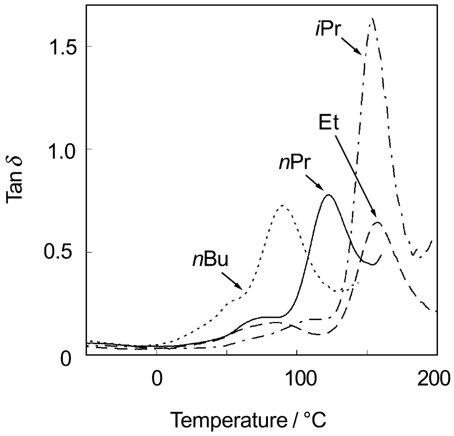


Fig. 2. Temperature dependence of loss tan δ of *disyndiotactic* polymers of ethyl, *i*-propyl, *n*-propyl and *n*-butyl crotonates at 1 Hz and a heating rate of 2 °C min^{-1}.

Table 2
Glass transition temperature (T_g) and decomposition temperature (T_d) of *disyndiotactic* polycrotonates and the corresponding syndiotactic polymethacrylates

Ester group	$\bar{M}_n$	Polycrotonates		Polymethacrylates	
		T_g (°C)	T_d (°C)	T_g (°C)	T_d (°C)
Me[a]	20,000	–	402	122	388
Et	56,000	157	399	55	374
i-Pr	73,000	149	365	51	330
n-Pr	71,000	116	397	46	348
n-Bu	90,000	90	395	22	362

T_d is defined as the temperature at which weight loss reaches 50% of the total weight loss in N_2.

[a] Taken from Ref. [16] (Table 1).

could not be molded to obtain a test specimen. Therefore, the direct comparison of the properties between PMeC and PMMA could not be made. Nevertheless, the mechanical property data were also collected for a commercial PMMA, since PMMA is the most important industrial material among polymethacrylates.

The values of Young's moduli of PEtC and P*i*PrC are comparable to that of PMMA, while those of P*n*PrC and P*n*BuC are much lower. P*i*PrC showed the highest tensile strength (31.8 MPa) among the polycrotonates, the value of which is still lower than that of PMMA. P*i*PrC also exhibited the highest Izod impact strength (1.6 kg cm^{-2}), which is comparable to that of PMMA.

Thus, among the polycrotonates examined, PEtC and P*i*PrC are hard and a little brittle materials, and particularly P*i*PrC has better balanced properties than PEtC.

The value of tensile elongation at break increased with increasing number of carbons in the ester group, consistent with the decreasing order of T_g values. In particular, P*n*BuC showed much larger elongation than the other polymers, while its tensile strength is the lowest, suggesting that P*n*BuC is a soft material.

One of the important characteristics of PMMA is its high transmissivity. Though, the chemical structures of polycrotonates and polymethacrylates are close to each other, PEtC and P*i*PrC showed rather low transmissivity as compared with P*n*PrC and P*n*BuC. The reason is not clarified yet but one possibility is the higher molding temperatures for PEtC (260 °C) and P*i*PrC (230 °C), at which the antioxidants added might be less effective to suppress coloring of the sample specimen.

Oxygen and nitrogen permeability coefficients of the polycrotonates are generally higher than those of PMMA, which are in the same orders of the reported value for pole(*sec*-butyl crotonate) [10] (O_2; 1.1×-10^{-9}, N_2; 2.9×-10^{-10}).

4. Conclusion

This work demonstrates that polycrotonates can be prepared directly and quantitatively with high molecular weight and narrow MWD by the GTP using HgI_2 catalyst and $(C_2H_5)_3SiI$ co-catalyst. Thermal stability of *disyndiotactic*polycrotonates is generally superior to that of polymethacrylates. One of the reason of distinctive properties is that *disyndiotactic* polycrotonates have stiffer main-chain. Among polycrotonates examined, P*i*PrC exhibited the highest Young's modulus, tensile strength and Izod impact strength, comparable to a commercial PMMA.

Acknowledgements

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Table 3
Mechanical properties of *disyndiotactic* polymers of ethyl, *i*-propyl, *n*-propyl and *n*-butyl crotonates and a commercial PMMA

Property	Polycrotonates				PMMA[a]
	Et	*i*-Pr	*n*-Pr	*n*-Bu	
Young's modulus/MPa	993	977	262	244	1006
Hardness[b]	79	83	72	58	91
Tensile strength/MPa	15.4	31.8	17.4	12.9	51.9
Izod impact strength/kg cm^{-2}	1.2	1.6	1.0	n.b.[c]	1.7
Tensile elongation at break/%	3.0	5.1	14.2	188	8.9
Density/g cm^{-3}	1.10	1.05	1.07	1.05	1.19
Refractive index	1.47	1.47	1.48	1.47	1.49
Transmissivity/%	70	64	85	89	90
Oxygen permeability coefficient (cm^3 cm cm^{-2} sec^{-1} cm Hg^{-1})	2.2×10^{-9}	1.1×10^{-9}	9.5×10^{-10}	2.1×10^{-9}	1.3×10^{-11}
Nitrogen permeability coefficient (cm^3 cm cm^{-2} sec^{-1} cm Hg^{-1})	2.0×10^{-9}	7.0×10^{-10}	2.9×10^{-10}	7.3×10^{-10}	3.8×10^{-11}

Test samples were obtained by molding in the presence of anti-oxidants.

[a] Measured in this work, using a commercially available PMMA[23] (Acrypet MF, Mitubishi Rayon Co., Ltd). The followings are the characteristics of the PMMA; $\bar{M}_n = 57,600$, $\bar{M}_w/\bar{M}_n = 1.61$, tacticity, *mm*:*mr*:*rr* = 14.6:41.4:44.0, $[\eta] = 0.53$ ($CHCl_3$, 25 °C).

[b] ASTM D2240 SHORE-D.

[c] Not break.

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