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Effect of branched alkyl groups on physical properties in poly(ethylene-*co*-branched alkyl methacrylate)s

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Summary

Poly(ethylene-co-5.4 mol% n-alkyl/branched alkyl methacrylate)s (PEM) were prepared by a dehydrogenchloride reaction of poly(ethylene-co-5.4 mol% alkyl methacrylic chloride) with the corresponding alkyl alcohol to investigate effect of branching structure and length of alkyl ester on a few physical properties of PEM [glass transition temperature (T_g), degree of crystallinity in polyethylene region (X_c) and dielectric molecular motion], where the alkyl groups used here are n-propyl, n-butyl, n-hexyl, n-decyl, 2-ethylhexyl, 3,5,5-trimethylhexyl and 2-(1',3',3'-trimethylbutyl)-5,7,7-trimethyloctyl. In the n-alkyl methacrylate copolymers, T_g and X_c were almost unchanged with the presence of alkyl ester, but T_g increased and X_c decreased in the highly branched alkyl methacrylate copolymers even at the low methacrylate content of 5.4 mol%.

Introduction

Recently, scientific and industrial interests are increased on polymers modified with a small amount of functional moiety to improve the physical properties of host polymers and create a new functional property. To date, a lot of modified polyethylenes have been extensively investigated; for example, low crystallinity polyethylene with various branched groups (1), ethylene ionomers which has a small amount of ionic groups as a pendant groups (2), liquid crystalline polymers (3) and so on. Low crystallinity polyethylenes have been developed by an introduction of α-branched olefins to ethylene chains; for example, copolymers of ethylene with various α-branched olefins such as propylene, butene, hexene and octene. In particular, the recent developments of polyethylene modified with bulky ring olefins such as norbornene arouse our attention to modified polyethylene (4). The purpose of this work is to prepare copolymers of ethylene with a small amount of branched alkyl methacrylates and to investigate their physical properties. It is investigated how the branching and length of alkyl groups affect glass transition temperature, molecular motion and crystallinity of polyethylene region. The alkyl esters and their denotations are listed in Table 1 and the chemical structures of three branched alkyl groups are shown in Figure 1.

Experimental

Poly(ethylene-co-5.4 mol% alkyl methacrylate)s were prepared by a dehydrogenchloride reaction of poly(ethylene-co-methacrylic acid chloride) with the corresponding alcohol as follows: Poly(ethylene-co-5.4 mol% methacrylic acid)(PEMA) is ACR-1560 of Mitsui-DuPont Polychemicals Co. Ltd., which is a random copolymer. The branched alkyl alcohols were supplied from Nisshin Oil Mills Ltd., Japan. A mixture of PEMA (100g), thionyl chloride (250ml) and benzene (750ml) was stirred for 5 h at 50 ℃ and the acid chloride of

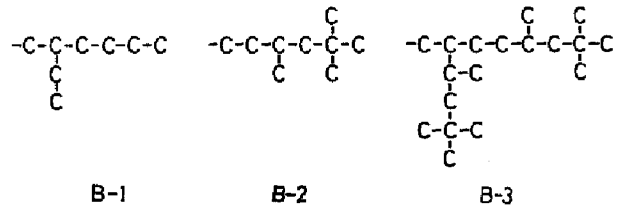

Fig.1. Structure of the branched alkyl chain.
B-1: 2-ethylhexyl
B-2: 3,5,5-trimethylhexyl
B-3: 2-(1',3',3'-trimethylbutyl)-5,7,7-trimethyloctyl

PEMA was obtained by fully evaporating the solvent and remaining thionyl chloride. The acid chloride was dissolved in benzene (550ml) and was mixed with the corresponding alcohol (1.5 mol), and then the mixture was refluxed for 8 h at 65 ℃. The crude alkyl ester was precipitated by pouring the reaction mixture into acetone. The alkyl ester was thoroughly purified by a precipitation method using soluble benzene and insoluble acetone solvents. All the polymers obtained were judged to be fully esterified by IR spectra; the peak near 1700 cm^{-1} and a broad peak at 2500~3000 cm^{-1}, which are attributed, respectively, to anti-stretching vibration of carboxylate and stretching vibration of OH in dimeric COOH group, disappeared by the esterification. Moreover, there appeared a peak near 1730 cm^{-1} which is attributed to C=O stretching vibration of the ester. Thermal measurements were made at a heating/cooling rate of 10 K • min^{-1} by use of a Seiko Denshi DSC 5000 differential scanning calorimeter (DSC). Dielectric constant (ε') and its loss (ε'') were measured by use of a multi-frequency LCR meter (YHP, Type 4274 A) at a heating/cooling rate of about 0.5 K • min^{-1} at several frequencies between 100 Hz and 100 kHz in the temperature range from 90 to 385 K. The three terminal electrode system was used as previously described (5). The sheets for dielectric measurements were about 0.5 mm thick and the diameter of main electrode was 37 mm, where gold was carefully deposited in vacuo on the surface of the sheet to ensure electrical contact between electrode and surface.

Results and discussion

Typical DSC curves are shown for B-1 in Figure 2. At the 2-nd heating run, there are observed two endothermic peaks near 337 and 357 K and one abrupt change near 216 K.

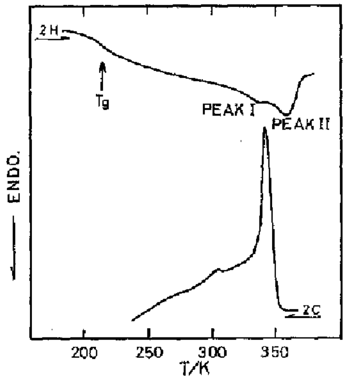

Fig.2. DSC thermogram for B-1.
2H: 2-nd heating, 2C: 2-nd cooling

Table 1 Melting point (T_m) and degree of crystallinity (X_c) for polyethylene crystallite region and glass transition temperature.

polymer	alkyl group	T_m(K)		X_c	T_g
		peak I	peak II	(%)	(K)
n-P	n-propyl	346	360	16.7	223
n-B	n-butyl	343	359	15.1	222
n-H	n-hexyl	331	359	14.6	216
n-D	n-decyl	340	356	13.6	218
B-1	2-ethylhexyl	337	357	14.8	216
B-2	3,5,5-trimethylhexyl	339	357	13.2	217
B-3	2-(1',3',3'-trimethylbutyl)-5,7,7-trimethyloctyl	330	355	7.3	227

The two peaks near 337 and 357 K are attributable to melting of bundle-like crystallites (6) and crystallites of polyethylene region, respectively, as well known, and the 216 K change is related to a glass transition (T_g). At the cooling run, a crystallization of polyethylene region was observed near 340 K. The degree of crystallinity in polyethylene region was estimated from the enthalpy change of two melting peaks, assuming that the melting enthalpy of polyethylene crystallite is about 290.4 J • g^{-1} (7). The thermal data are listed in Table 1 for all the polymers used here.

In Figure 3, the values of T_g are plotted against carbon no. of alkyl groups (n), where n is carbon no. of main (longest) methylene chains in the branched alkyl esters. As shown in Figure 3, T_g in the conventional poly(n-alkyl methacrylate)s (8,9) clearly decreases with the increase of n, which has been explained by a plasticization effect of flexible alkyl chains; it has been pointed out that as n increases, the neighbouring chains are pushed further apart, resulting in making the motion of backbone chains easier. In the branched alkyl esters, on the other hand, it has been reported that T_g sometimes shifts back to higher temperatures, because of an increase of steric hindrance to intramolecular rotations produced by the more rigid branched alkyl substituent; for example, T_g of poly(isobutyl methacrylate) is higher by

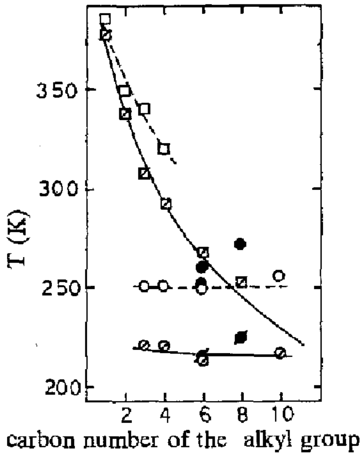

Fig.3. Plots of T_g and T_{max} versus carbon number of the alkyl group (8,9)
□, ▨: poly(n-alkyl methacrylate) (conventional)
○, ⊘: poly(ethylene-co-n-alkyl methacrylate)
●, ●: poly(ethylene-co-branched alkyl methacrylate)
—— : T_g, ----- : T_{max} at 1 kHZ

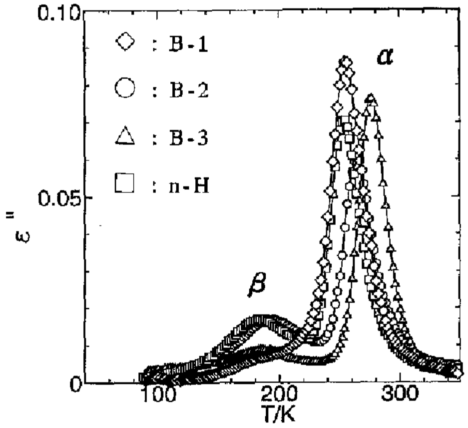

Fig.4. Temperature dependence of dielectric loss (ε ") at 1 kHz.

45℃ (9) than that of poly (n-butyl methacrylate) (9,10). In the present poly(ethylene-co-n-alkyl methacrylate)s, T_g scarcely changes with n, which means too low content of alkyl esters (about 5.4 mol%) to affect T_g, but T_g of B-3 is larger by about 10℃ than that of B-1. It is of interest that the very bulky alkyl ester like B-3 affects T_g even in the low content of the ester.

Figure 4 shows temperature dependences of dielectric loss (ε ") at 1 kHz for four polymers. In all the polymers, there are observed two relaxations, α at 250~270 K and β at 180~190 K. It is well known that the α relaxation is related to a glass transition, while the β relaxation is due to a local motion of ester groups below T_g. As the alkyl group is more highly branched, the temperature exhibiting the peak top of ε " (T_{max}) somewhat increasses, as seen in Figure 3.

Arrhenius plots of two relaxations are shown in Figure 5 for all the polymers. In all the polymers, the plots show a straight line for the β relaxation but are curved for the α

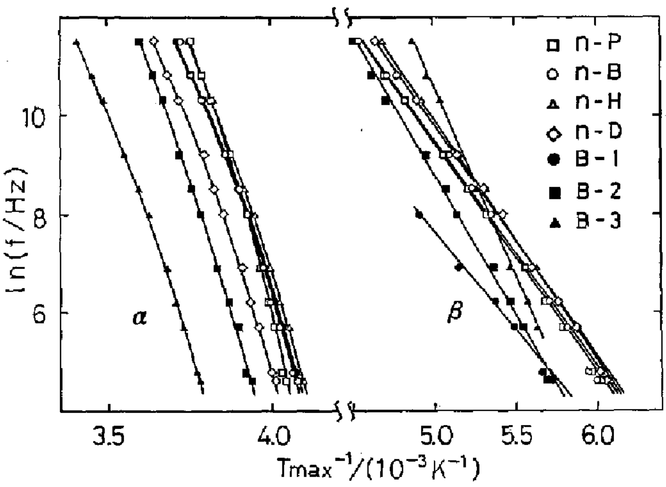

Fig.5. Arrhenius plots of α and β relaxations.

relaxation, obeying WLF equation,

$$\log f(T)=C_1+\log f(T_g)-C_1C_2/(T-T_g-C_2)$$

The relaxation parameters of α and β relaxations are listed in Table 2.
The free volume at T_g (f_g) are between 0.018 and 0.023, indicating that the α relaxation obeys the WLF process. On the other hand, the activation enthalpy of β relaxation ($\triangle H$) is about 39 kJ · mol^{-1} for n-alkyl esters but become larger, as the alkyl group is more branched, being about 62 kJ · mol^{-1} for B-3. This result suggests that the highly bulky alkyl groups hinder the rotational motion of the ester groups.
The degree of crystallinity (X_c) slightly decreases with increasing the length of alkyl group (n), but largely decreases in the highly branched esters (B-3). It is noted that the bulky branched alkyl ester groups disturb the crystallization of polyethylene region even in the low MAA content of 5.4 mol%.
In conclusion, this work indicates that only the highly branched alkyl esters can affrod some change in the physical properties such as T_g and degree of crystallinity in poly(ethylene-co-alkyl methacrylate)s with the low alkyl methacrylate content of 5.4 mol %.

Table 2 Relaxation parameters for α and β relaxations.

polymer	α relaxation				β relaxation	
	T_{max} (K) at 1 kHz	C_{1g}	C_{2g}	f_g	T_{max} (K) at 1 kHz	$\triangle H$ (kJ · mol^{-1})
n-P	252	23.4	14	0.019	180	38
n-B	251	18.7	20	0.023	180	39
n-H	250	22.9	17	0.019	178	39
n-D	256	24.2	19	0.018	179	39
B-1	251	22.1	21	0.020	194	33
B-2	261	24.0	27	0.018	186	46
B-3	272	24.7	22	0.018	183	62

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