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Copolymerization of methyl α-(chloromethyl)acrylate with styrene accompanied by addition-fragmentation chain transfer

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SUMMARY

Copolymerization of methyl α-(chloromethyl)acrylate (MCMA, M_1) as homopolymerizable addition-fragmentation chain transfer (AFCT) agent with styrene (St, M_2) was investigated. The monomer reactivity ratios were $r_1 = 0.12$ and $r_2 = 0.18$ at 60° C indicating high alternating tendency. The copolymers bearing the 2-carbomethoxy-2-propenyl ($CH_2{=}C(CO_2Me)CH_2$-) ω-end group formed by AFCT were submitted for ^{1}H-NMR structural analysis. The M_n of copolymer and contribution of AFCT as end forming reactions decreased and increased with increasing MCMA content in comonomer, respectively. The propenyl end groups bound to the St and MCMA units were separately detected. Furthermore, it was concluded that the MCMA-St copolymerization involves not only AFCT but also chlorine abstraction by the poly(St) radical.

INTRODUCTION

α-(Substituted methyl)acrylic esters functioning as chain transfer agents through the addition-fragmentation (AFCT) mechanism have been employed for efficient control of molecular weight and ω-end structure of polymer [1-8]. ^{1}H-NMR structural analysis of homopolymers of styrene (St) [5,7], methyl methacrylate (MMA) [5,7], and methyl acrylate [5], and St-MMA copolymer formed in the presence of methyl α-(bromomethyl)acrylate (MBMA) [9] has revealed that 2-carbomethoxy-2-propenyl group (***E***) is almost quantitatively introduced because of sufficiently fast addition of propagating radical to MBMA followed by fast fragmentation of MBMA radical. Minor reactions of AFCT agent would compete with AFCT [10,11]. Homopolymerization of MBMA was observed during the oligomer formation of common monomers in the presence of a large amount of MBMA [12]. Furthermore, methyl α-(chloromethyl)acrylate (MCMA) [13] as well as α-(phenoxymethyl)- [14] and α-(2-carbomethoxyl)acrylates [15,16] have been known as polymerizable AFCT agents, resulting in introduction of ***E*** at the ω-ends less efficiently than MBMA.
Recently, it has been reported that some of polymer chains bearing ***E***s are as reactive as common monomers [17]. AFCT has drawn attention as an efficient method to prepare a radically copolymerizable macromonomer by radical chain polymerization, and the ***E*** introduction by AFCT in competition with elementary reactions should be

studied in more detail. In this paper, copolymerizations of MCMA with St and $CH_2=CHC_6D_5$ (St-d_5) were carried out to shed light on competition of propagation and chain transfer. The end structures of copolymer were studied by ^{1}H-NMR spectroscopy to reveal the reaction modes of MCMA.

EXPERIMENTAL

MCMA was prepared and purified as reported [18]. St was distilled under reduced pressure before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. St-d_5 and $CD_2=CDC_6H_5$ (St-d_3) were synthesized by dehydration of $CH_3CH(OH)C_6D_5$ and $CD_3CD(OH)C_6H_5$, respectively [19]. Copolymerizations were carried out in glass tubes degassed via consecutive freeze-pump-thaw cycles and sealed under vacuum. After polymerization, the contents of the tube were poured into a large amount of methanol to isolate copolymer. The ^{1}H-NMR resonances of the main chain CH and CH_2 at 1.0-2.3 ppm (St unit + MCMA unit), the CH_2Cl and OMe at 2.6-4.2 ppm (MCMA unit), and phenyl protons (St unit) were chosen for calculation of copolymer composition. Compositions of MCMA-St-d_5 copolymers were calculated from the intensities of the peaks due to the CH_2 and CH (MCMA unit + St-d_5 unit) and those due to the CH_2Cl and OMe (MCMA unit). Assignments of the resonances ascribed to the CH_2 and CH (MCMA unit + St unit) were confirmed by comparison of the ^{1}H-NMR spectrum of MCMA-St-d_5 copolymer with that of MCMA-St-d_3 copolymer. Monomer reactivity ratios (r_1 and r_2) were evaluated by a nonlinear least squares procedure [20]. GPC measurements were carried out using a Tosoh 8000 series high-performance liquid chromatograph equipped with TSK-gel columns for GHC. The molecular weight was calibrated by poly(St) standards. ^{1}H-NMR spectra were recorded on a JEOL JNM-A 400 spectrometer at 400 MHz. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively.

RESULTS AND DISCUSSION

MCMA-St and MCMA-St-d_5 copolymers

The copolymerization of MCMA (M_1) and St or St-d_5 (M_2) was carried out in benzene at 60 °C: $r_1 = 0.12$ and $r_2 = 0.18$ for MCMA (M_1)-St (M_2), and $Q_1 = 1.13$ and $e_1 = 1.20$. The r_1 and r_2 values for MCMA (M_1)-St-d_5 (M_2) copolymerization were 0.13 and 0.27, respectively. The results of the copolymerizations are shown in Table 1. Actually, nuclear deuteration of St did not affect copolymer composition. The copolymerizations of St and St-d_5 gave similar conversions and M_ns at the respective comonomer compositions. The M_n decreased with increasing MCMA content in comonomer in accordance with the AFCT function of MCMA.

Structures of copolymer end

The olefinic protons of ***E*** exhibited much weaker resonances than the characteristic resonances due to the monomeric units. Expanded ^{1}H-NMR spectra at 5.0-6.5 ppm are shown in Figure 1. The ***E*** content in copolymer ([MCMA unit]/[***E***]) was obtained using the intensity ratio of the resonances of the OMe and the unsaturated methylene protons [13]. However, some of the resonances due to ***E*** were hidden by the very

Table 1. Copolymerizations of MCMA (M_1) with St and St-d_5 (M_2)[a]

[MCMA] in comonomer (mol%)	Time (h)	Copolymer with St		Copolymer with St-d_5			
		[St] (mol%)	M_n(G)	[St-d_5] (mol%)	M_n(G)	M_n(N)[b]	M_n(G)/ M_n(N)[c]
10	3	71.7	48300	75.0	47000	337600	0.14
30	3	58.1	52200	61.7	48000	185700	0.26
50	4	57.2	48100	54.0	44000	89400	0.49
70	5	46.2	27500	44.8	22500	34200	0.66
90	6	32.5	9200	33.6	9600	18000	0.53
100	4	0	4400[d]	-	-	-	-

[a] $[M_1] + [M_2] = 3.0$ mol/L, [AIBN] = 5 mmol/L. [b] Calculated from the ***E*** content determined by ^{1}H-NMR specctroscopy. [c] Efficiency of the ***E*** introduction. [d] M_n determined by vapor pressure osmometer (M_n(V)), and $M_n(V)/M_n(N) = 1.05$ from ref. 13.

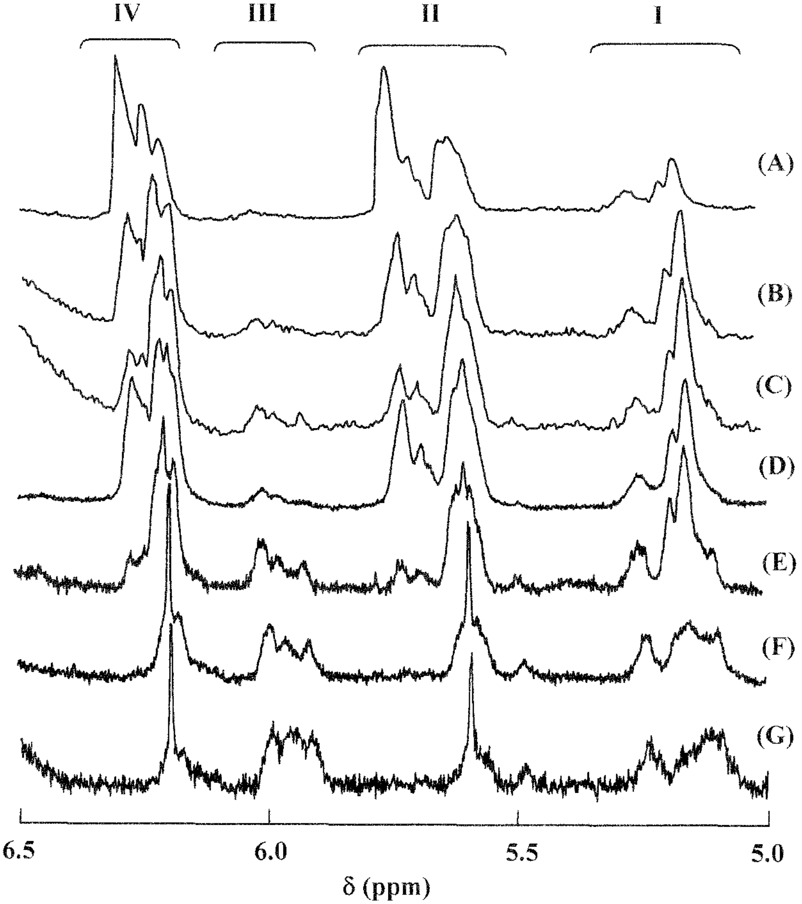


Figure 1. Expanded ^{1}H-NMR spectra of ***E*** bound to MCMA-St copolymers containing 26.3 (A), 32.5 (B), and 39.3 mol% (C) of St unit, and MCMA-St-d_5 copolymers containing 33.6 (D), 44.8 (E), 54.0 (F), and 61.7 mol% (G) of St-d_5 units.

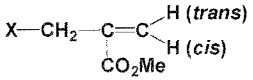
Table 2. Intensities of the individual resonances at 5.0-6.4 ppm

[St] or [St-d_5] in copolymer (mol%)	Relative intensity[a] (%)				100 × **I**/(**I** + **II**)[b] (%)	**I** – **III**[c] (%)
	I (5.0-5.3 ppm)	**II** (5.5-5.8 ppm)	**III** (5.9-6.1 ppm)	**IV** (6.1-6.3 ppm)		
26.3[b]	14	43	2	41	25	12
32.5[b]	23	37	4	36	38	19
33.6[c]	23	37	3	37	38	20
39.3[b]	25	35	6	34	42	19
44.8[c]	32	28	9	31	53	24
54.0[c]	33	25	19	23	57	14
61.7[c]	35	18	31	16	66	4

[a] Spectral intensities of **I-IV** relative to (summation of **I-IV** intensities). [b] Content of (St-Cl+St-***E***) relative to (St-***E***+MCMA-***E***+St-Cl). [c] Content of St-Cl relative to (St-***E***+MCMA-***E***+St-Cl). [d] [St unit] in copolymer. [c] [St-d_5] unit] in copolymer.

intense resonances due to the phenyl group when the copolymer contained more than 40 mol% of St. To overcome this problem, St-d_5 was copolymerized with MCMA. The M_ns calculated from [MCMA unit]/[E] with consideration of copolymer composition (M_n(N)) are considerably greater than the M_ns measured by GPC (M_n(G)) as summarized in Table 1. M_n(G)/M_n(N) indicating the efficiency of the end group introduction decreased with increasing MCMA content in comonomer because of the AFCT function of MCMA. The [MCMA unit]/[E] value for the poly(MCMA) was 33.2 corresponding to M_n(N) = 4600 close to M_n(V) = 4400 because of almost quantitative introduction of ***E*** [13]. Usually, M_n(N) tends to be slightly higher than M_n(G) when M_n was controlled by AFCT [5,10,17]. Difference between M_n(N) and M_n(G) can be explained by contributions of bimolecular termination, and addition of poly(St) radical to ***E*** followed by coupling with the polymer radical and/or addition to St [15]. In the case of the MCMA-St copolymerization, poly(MCMA) radical would rapidly add to St to diminish the AFCT contribution.

The resonances in Figure 1 can be grouped as **I-IV**, and the intensities of **I-IV** relative to the total of the intensities of **I-IV** are summarized in Table 2. The olefinic protons of ***E*** bound to poly(St) (5.08 and 5.92 ppm) and poly(MCMA) (5.74 and 6.27 ppm) chains exhibit different chemical shifts depending on the *cis*- or *trans*-H with respect to the CO_2Me group [13,21]. Figure 2 shows a linear relationship between the chemical shifts of the *cis*- and *trans*-Hs in monomers, polymers or oligomers given by a generalized structure **1**. A pair of resonances assigned to the *cis*- and *trans*-H can be predicted among the resonances at 5.0-6.5 ppm, if the resonance of either *cis*- or *trans*-H is assigned. Apparently, an increase in electronegativity of X would result in lower magnetic field shifts of the resonances ascribed to the olefinic protons.



$$X{-}CH_2{-}C(CO_2Me){=}C\begin{matrix}H\ (trans)\\ H\ (cis)\end{matrix}$$

1

The resonances due to ***E*** appear as two sets of two lines depending on the adjacent monomeric unit in the spectra of MMA-MCMA copolymer [13] and the St-MMA copolymer obtained in the presence of MBMA [9]. However, **I-IV** apparently consist of some additional resonances which relative intensities seem to be depend on copolymer composition. It was suggested that the chemical shifts of the resonances

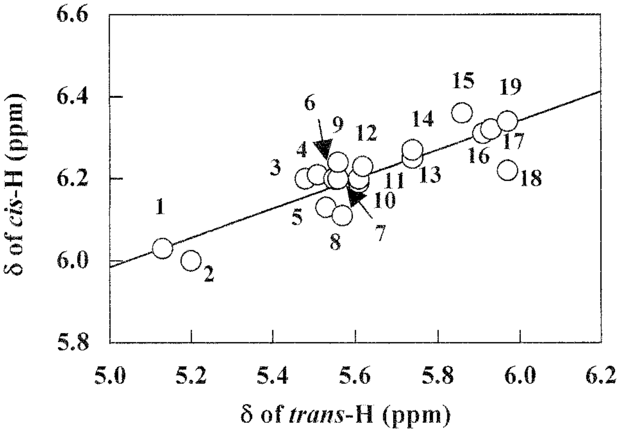
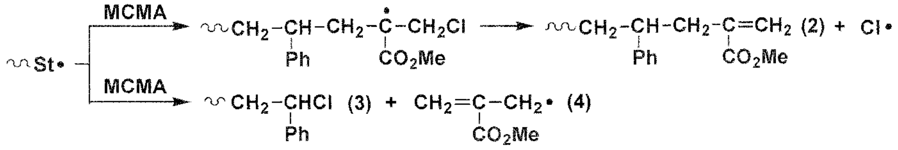


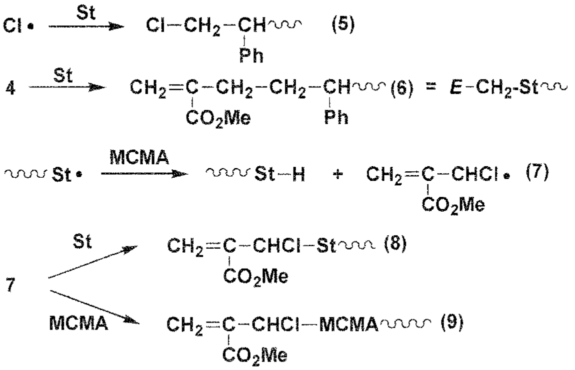
Figure 2. Linear relationship between chemical shifts of *cis*- and *trans*-Hs of **1**: X = $C(Me)_2Ph$ (1)[21], poly(St) (2)[9], poly(MMA) (3)[5], $C(Me)_2CO_2Me$ (4)[21], Me (5)[22], poly(methyl α-[2,4-dicarbomethoxybutyl]acrylate) (6)[23], poly(MA) (7)[5], H (8), poly[methyl α-(2-carbomethoxyethyl)acrylate] (9)[15], CH_2CO_2Me (10)[15], $CH(CO_2Me)CH_2CH_2CO_2Me$ (11)[23], $CH(CO_2Me)_2$ (12)[24], $C(CO_2Me)_3$ (13)[25], poly(MCMA) (14)[13], OCOMe (15)[24], OEt (16)[27], OCH_2Ph (17)[9], OPh (18)[14], Br (19)[5].



Scheme 1

consisting of **I-IV** are primarily governed by the adjacent monomeric unit to ***E*** and the penultimate unit also affect to a smaller extent.

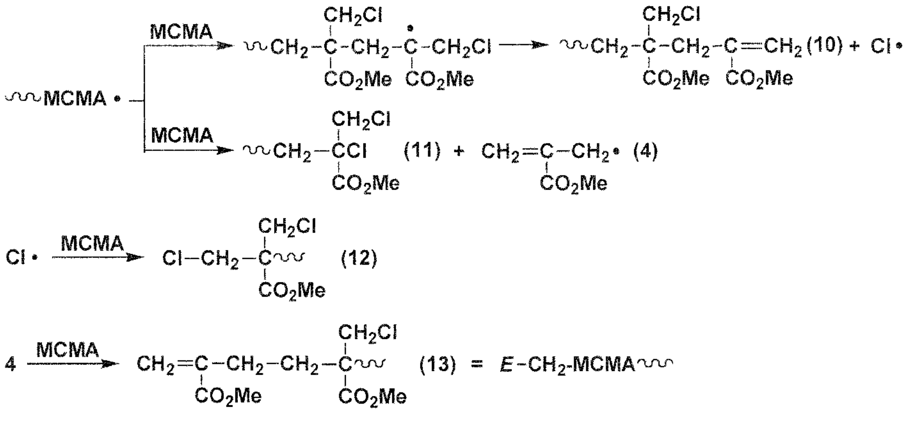
Based on Figure 2, **I** and **III** are assigned to the *trans*- and *cis*-H of **2** arising from AFCT as in Scheme 1. The intensity of **I** increased with increasing St unit content to a certain extent. The intensity of **I** decreased by a further increase in the St content in copolymer and became almost the same with that of **III** at high St-d_5 unit contents. Although singlets were considered to be involved in **I**, no resonances paired with the singlets in **I** were not detected in **III**. One of the possible origins of the singlets of **I** would be the benzylic protons of **3** which may be formed by chlorine abstraction from MCMA as in Scheme 1. The resonance due to the $ClCH_2$ of **5** would not be involved in Figure 1. Addition of **4** to St would result in **6** (Scheme 2) to show a pair of resonances in conformity with the linear relationship in Figure 2. However, resonances due to **2** and **6** might not be observed separately because of the non-polar nature of poly(St) chain. The content of (St-Cl + St-*E*) which was calculated from the intensity ratio of **I** to (**I** + **II**) is approximately equal to the St content in copolymer was, and the St-Cl content was given by (**I** – **III**) in Table 2. Alternatively, MCMA might be feasible to hydrogen abstraction by poly(St) radical to form **7** which might add to St and MCMA to give **8** and **9**. The α-end structure involving **8** should exhibit the resonance due to the *cis*-olefinic proton at lower magnetic fields than 6.4 ppm according to Figure 2 because of the presence of the ClCH group. No resonance was detected at the chemical shift range to exclude the hydrogen abstraction from MCMA. Chlorine or hydrogen abstraction from the CH_2Cl in the copolymer can be ruled out



Scheme 2

because of no allylic stabilization of the radical formed. **III** is ascribed to the *cis*-H of *E* bound to St unit (St-*E*) involving at least two signals occurring to the significant change in intensity in Figure 1, and the component of the same intensity with **III** would be involved in **I** as the resonances assigned to the *trans*-H of St-*E*. St-*E* with the MCMA penultimate unit (MCMA-St-*E*) is expected to exhibit the resonances of the *cis*- and *trans*-H at slightly greater chemical shifts than those of St-*E* bearing the St penultimate unit (St-St-*E*) because of weaker electron withdrawing character of St unit than MCMA unit.

II and **IV** are unambiguously assigned to the *trans*- and *cis*-Hs of *E* bound to MCMA unit (MCMA-*E*), respectively, formed as **10** in Scheme 3, and **II** and **IV** show the same intensity at each copolymer composition (Table 2). Polar factors of MCMA and chlorine atom would suppress formations of **11** and **12**. The CH_2Cl group of **11** and **12** could not be detected by ^{1}H-NMR spectroscopy because of the presence of the stronger resonances due to the CH_2Cl and OMe of the repeating units. **II** and **IV** would also involve the resonances ascribed to *E* of **13** arising from addition of **4** to MCMA. The resonances due to **13** with the St penultimate unit might overlap with those due to **10** with the same penultimate unit. The resonances due to **13** with the MCMA penultimate unit would appear at slightly higher magnetic field than those due to **10** with the MCMA penultimate unit in **II** and **IV** because the *E* bound to the α-



Scheme 3

Table 3. Effects of St content in copolymer on spectral intensity of individual resonances and assignment of **I-IV**

Notation	δ (ppm)	Increase in [St] in copolymer[a]	No.[b]	Assignment
I	5.10	Increase	**2**	~St-St-*E*-trans
I	5.15	-[c]	**3**	~St-St-Cl[d]
I	5.18	-[c]	**3**	~MCMA-St-Cl[d]
I	5.25	Increase	**2**	~MCMA-St-***E***-*trans*
II	5.60	Increase	**10**	~St-MCMA-***E***-*trans*
II	5.69	Decrease	**13**	~MCMA-MCMA-CH_2-***E***-*trans*[e]
II	5.72	Decrease	**10**	~MCMA-MCMA-***E***-*trans*
III	5.93	Increase	**2**	~St-St-***E***-*cis*
III	6.00	Increase	**2**	~MCMA-St-***E***-*cis*
IV	6.20	Increase	**10**	~St-MCMA-***E***-*cis*
IV	6.22	Decrease	**13**	~MCMA-MCMA-CH_2-***E***-*cis*[e]
IV	6.27	Decrease	**10**	~MCMA-MCMA-***E***-*cis*

[a] Change in intensity relative to the total of the resonances in 5.0-6.4 ppm. [b] Structures in Schema 1-4. [c] Dependence of spectral intensity on copolymer composition exhibited maximum, see Figure 1 and Table 2. [d] Benzyl proton. [e] Formed by initiation with **4**.

carbon of MCMA in **10** and the β-carbon in **13**. Table 3 summarizes the relevant assignments of the individual resonances to the end structures consisting of two monomer units and ***E*** or Cl. In this table, "Increase" and "Decrease" denote changes in spectral intensity of the resonances as shown in Figure 1.

MCMA-St and MCMA-MMA copolymers

Why the penultimate unit affects the chemical shifts of the protons of ***E*** bound to MCMA-St copolymer unlikely to ***E*** bound to MCMA-MMA copolymer. One of the possibilities could be more significant difference between the effects of MCMA and St units as adjacent and penultimate units on the chemical shifts of the olefinic protons of ***E*** in comparison with that between the effects of MCMA and MMA units as can be predicted from Figure 2. Two types of chain transfer, AFCT and chlorine abstraction from MCMA by poly(St) radical, were found to be involved resulting in four groups of lines and one group of lines at 5.0-6.5 ppm. However, the copolymerization of MCMA-MMA (r_{MCMA} = 0.56, r_{MMA} = 1.53) involved only one type of chain transfer, AFCT [13]. Resonances such as those due to MMA-CH_2-***E*** suggesting chlorine abstraction by poly(MMA) radical were not founded in the ^{1}H-NMR spectra of the copolymers. It was deduced from the monomer reactivity ratios that faster homopropagation of MMA than that of St reduces the contribution of chlorine abstraction from MCMA and that electron accepting character of poly(MMA) radical unlikely to electron donating character of poly(St) radical suppresses chlorine abstraction. Thus, all the factors relating to MMA and poly(MMA) radical tend to suppress chlorine abstraction in the MCMA-MMA copolymerization.

CONCLUSIONS

The copolymerizations of MCMA (M_1)-St (M_2) (r_1 = 0.12 and r_2= 0.18) and MCMA (M_1)-St-d_5 (M_2) (r_1 = 0.13 and r_2 = 0.27) exhibited a highly alternating tendency in contrast to the MCMA-MMA copolymerization [13]. The MCMA-MMA copolymerization yields the copolymers bearing ***E***, and the olefinic protons of ***E*** bound to MCMA and MMA units show two sets of two line spectra. However, the chemical shifts of the unsaturated methylene protons of ***E*** bound to the MCMA-St copolymer were affected by not only the *cis*- or *trans*-positions with respect to the CO_2Me group but also the monomer units including the MCMA penultimate unit bound to ***E***. MCMA could not be a perfect AFCT agent in copolymerization with St because of fast addition of poly(MCMA) radical to St as observed as high alternating tendency. Furthermore, the copolymerization of MCMA with St was found to involve AFCT and chlorine abstraction from MCMA by poly(St) radical. The contribution of the chlorine abstraction depended on comonomer composition; less than 5% of the total of the ω-end groups at more than 70 mol% of St or St-d_5 in comonomer or more than 60 mol% of St or St-d_5 unit in copolymer.

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