also dynamically extinct under the rules given by Gjonnes and Moodie.[13] They may, however, be observed under several conditions: a slight misalignment of the crystal, an imperfectly flat crystal, or if there is multiple incoherent scattering. Their presence is thus consistent with the $P2_1/n$ designation in this case.

Discussion

The two experimental difficulties encountered when recording three-dimensional electron diffraction patterns arise from the short life span of the radiation-sensitive polymeric crystals. The difficulties are, first, how quickly and accurately one orients a crystal so that one of the crystallographic axes is coincident with the tilt axis of the goniometer and, secondly, finding the proper tilt angle to have the diffraction spots of the zone of interest exactly in the recording plane. An examination of the electron diffraction patterns of the *hkh* and *h*,*k*,2*h* zones of poly(*t*-CDS) (Figure 2a of ref 11) indicates that these experimental problems have not been perfectly resolved. In spite of the problems described above, the electron diffraction data from poly(*t*-CDS)[11] provide consistent results in each zone studied. The three different microcrystals appear to have each a slight bend of about 2°. The diffracted beam amplitudes from these very thin crystals are slightly affected by dynamical scattering, confirming that the kinematic structure analysis of Brisse, Rẽmillard, and Chanzy[11] is appropriate.

Three-dimensional electron diffraction data can be obtained from radiation-sensitive organic microcrystals and reliable structure amplitudes deduced when radiation damage is minimized[11] and crystal morphology and diffraction conditions are taken into account. Their utility for structure analysis has been demonstrated.[11]

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Registry No. (*trans*-1,4-Cyclohexanedimethanol)·(succinic acid) (copolymer), 81381-36-4; poly(*trans*-1,4-cyclohexanediyldimethylene succinate) (SRU), 81381-32-0.

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Radical Reactivity and Q–e Values of Methyl α-(Trifluoromethyl)acrylate

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Introduction

Analogues of poly(methyl methacrylate) (PMMA) incorporating halogen atoms in the α-position or in the ester side group have recently attracted much attention as sensitive electron-beam positive resists. Ito et al. have reported that methyl α-(trifluoromethyl)acrylate (MTFMA) does not undergo radical homopolymerization but readily polymerizes by pyridine initiation due to the low electron density on the double bond.[1] Radical copolymerization of MTFMA (M_1) with MMA (M_2) has been analyzed and yielded the monomer reactivity ratios of $r_1 = 0$ and $r_2 = 2.36$. Giese et al. have directly measured the substituent effect on the rate of addition of alkyl radicals to polymerizable alkenes by the "mercury method" (Scheme I)[2] and found that the rate constant of the cyclohexyl radical addition experimentally determined, k_{rel} (relative to styrene), is correlated to the Alfrey–Price Q–e parameters[3] as expressed by the following equation.[4]

$$\log k_{\mathrm{rel}} - \log Q_j = 0.5 + 0.825e_j \tag{1}$$

Here the subscript j denotes a jth monomer.

Now we report the relative rates of the alkyl radical addition to MTFMA as well as Q and e values of MTFMA determined by combination of the copolymerization analysis and the mercury method. The Q and e parameters cannot be determined from only the monomer reactivity ratios in this case because $r_1 = 0$.

Experimental Section

Materials. MTFMA was custom synthesized by Parish Chemicals according to the method previously described.[1] Copolymerization of MTFMA with MMA and determination of the monomer reactivity ratios have been previously reported.[1]

Reaction of MTFMA with Cyclohexylmercuric Chloride. To a solution of 2.33 g (7.3 mmol) of cyclohexylmercuric chloride (**1**) and 1.97 g (14.6 mmol) of MTFMA (**2**) in 50 mL of dichloromethane was added 700 mg (14.6 mmol) of $NaBH_4$ in 5 mL of water at 20 °C. After 30 min, the reaction mixture was dried over $MgSO_4$ and distilled at 115 °C (bath temperature)/12 mmHg to give 1.36 g (79%) of the product **3**: IR 1750 (C═O), 1040 cm^{-1} (C–F); ^{1}H NMR (300 MHz) δ 0.78–1.96 (m, 13 H, $C_6\mathit{H}_{11}C\mathit{H}_2$), 3.13–3.31 (m, 1 H, $C\mathit{H}CO_2CH_3$), 3.77 (s, 3 H, $CO_2C\mathit{H}_3$). Anal. Calcd for $C_{11}H_{17}F_3O_2$: C, 55.45; H, 7.19. Found: C, 55.27; H, 7.13.

Kinetics. To a mixture of 64 mg (0.20 mmol) of cyclohexylmercuric chloride (**1**) and at least a 10-fold excess of MTFMA (**2**) and acrylonitrile (AN) (**4**) in 10 mL of dichloromethane was added 10 mg (0.3 mmol) of $NaBH_4$ in 1 mL of water at 20 °C.

Results and Discussion

When generation of the cyclohexyl radical from $C_6H_{11}HgCl$ and $NaBH_4$ is carried out in the presence of MTFMA, the adduct radical $C_6H_{11}CH_2\dot{C}(CF_3)CO_2Me$ captures H to give the product **3** in almost quantitative yield (80–95%), as is the case with many other olefinic monomers.[5] This quantitative addition of the cyclohexyl radical to the β-carbon of the olefinic double bond warrants

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Scheme I
Mercury Method

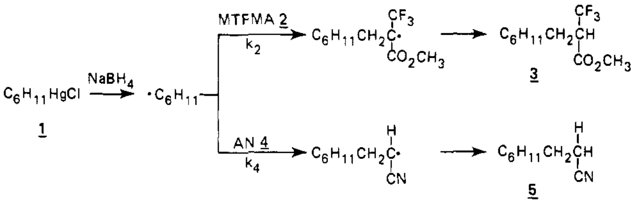

Table I
Competitive Addition of MTFMA and AN to Cyclohexyl Radical in Dichloromethane at 20 °C

feed, mmol		feed ratio	product ratio
MTFMA (2)	AN (4)	[4]/[2]	[5]/[3]
2.13	11.32	5.31	0.58
2.14	20.56	9.61	0.96
2.16	29.74	13.77	1.33
2.14	37.75	17.64	1.61
2.23	46.43	20.82	1.74
2.04	57.40	28.14	2.37

After 30 min, the mixture was filtered and dried over $MgSO_4$, and the solvent was distilled off. The ratio of the products 3 and 5 was determined by gas chromatography (Perkin-Elmer, Sigma 3, Dexil 10%, 2 m).

the use of the mercury method as a model reaction of the propagation step in the radical copolymerization. In Table I are summarized the results of the competitive addition of MTFMA and AN to the cyclohexyl radical, and Figure 1 demonstrates the pseudo-first-order plot of the product ratio [5]/[3] vs. the feed ratio [4]/[2]. The slope of the linear plot (0.089) corresponds to the ratio of the rate constant k_4 to the rate constant k_2, indicating that MTFMA is about 11 times more reactive than AN toward the electron-rich cyclohexyl radical. Since MMA is about 4.8 times less reactive than AN,[6] MTFMA is 54 times more reactive than MMA toward the cyclohexyl radical in dichloromethane at 20 °C. The experimental analysis was made on the pair of MTFMA and AN instead of MMA, because the direct reactivity comparison of the MTFMA–MMA system was believed to be difficult due to the great difference in the reactivity. The relative reactivity of MTFMA agrees fairly well with the linear correlation between log k_{rel} and Hammett σ of the substituent on the α-position of methyl acrylate analogues.[6]

Though it is usually possible to calculate Q and e values from the monomer reactivity ratios, the MTFMA–MMA system cannot be treated in that fashion because r_1 is zero. However, the combination of the equation (1) where $k_{\mathrm{rel}} = 264$ and $r_2 = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)] = 2.36$ allows us to calculate the Q and e values of MTFMA as 0.74 and 2.50, respectively, based on the known parameters of MMA ($Q_2 = 0.74$ and $e_2 = 0.40$). The r_1 can be now back-calculated to be 0.005, very close to the experimentally determined value of 0.[1] The calculation may suggest that the resonance stabilization factors of MTFMA and MMA are the same and the reactivity difference can be interpreted in terms of the great difference in the polar effect. The very large e value of MTFMA (2.5) prevents the monomer from homopolymerizing by radical initiation.[1,7] Because our separate investigation indicates that primary radicals from BPO or AIBN add to the β-carbon of MTFMA,[8] the resistance to the radical homopolymerization must be ascribed to the absence of the propagation step, which may arise from the lack of interaction between the singly occupied molecular orbital (SOMO) of the MTFMA radical and the lowest unoccupied molecular orbital (LUMO) of the MTFMA monomer due to a very low SOMO energy of the radical. However, further work is required to unambiguously explain the phenomenon.

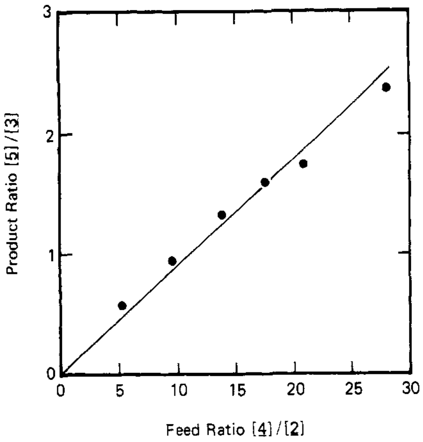

Figure 1. Correlation between the product ratio and the feed ratio in the cyclohexyl radical addition in dichloromethane at 20 °C.

Linear relationships between vinyl monomer reactivity and NMR chemical shifts and between e values and chemical shifts have been well established. Although the β-carbon resonance of MTFMA at 133.2 ppm well explains the large e value and low electron density of the monomer at least qualitatively (compare with 125.0 ppm of MMA), the quantitative agreement of our data with the linear relationship between the ^{13}C chemical shifts and e values proposed by Herman and Teyssie[9] and with that between ^{13}C chemical shifts and log $(1/r_2)$–log Q_1 proposed by Hatada et al.[10] is still not satisfactory. The multiple-correlation analysis program proposed by Borchardt and Dalrymple[11] to generate equations relating the Q–e values to the ^{13}C chemical shifts also failed to give meaningful results, which may be ascribed to the steric effect.[12] Although our copolymerization analysis combined with the mercury method indicates that the reactivity of MTFMA may be explained in terms of the polar substituent effect in the first approximation, it is not yet clear whether the steric effect of the CF_3 group ($E_s = -1.16$) is negligible or plays a significant role.

Registry No. 1, 24371-94-6; 2, 382-90-1; 4, 107-13-1; MMA, 80-62-6.

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