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Copolymerization of 2,4,5-Trichlorophenyl Acrylate with Styrene: Reactivity Ratios, Molecular Weights, and ^{13}C NMR Spectra

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ABSTRACT: The free radical copolymerization of 2,4,5-trichlorophenyl acrylate (M_1) with styrene (M_2) in chlorobenzene and in the presence of α,α'-azobisisobutyronitrile (AIBN) at 60 °C is reported. ^{13}C NMR spectra of M_1, the homopolymers of M_1 and M_2, and an equimolar copolymer of M_1 and M_2 are given. Copolymer compositions of ten copolymer samples obtained from feed ratios of M_1:M_2 = 7:93 to 92:8 were determined by chlorine analysis. The reactivity ratios were estimated by the Kelen and Tudos method to obtain r_1 = 0.29 ± 0.03 and r_2 = 0.25 ± 0.03. The effect on molecular weights of initiator concentration, extent of monomer conversion, and feed composition is also discussed. The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights were determined by gel permeation chromatography. $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values for the homopolymers at low (~4%) conversion were 20 350 and 2.0 for M_1 and 43 700 and 1.69 for M_2. The corresponding values for a copolymer formed from an equimolar monomer concentration ($[M_1] + [M_2]$ = 0.81 mol dm^{-3}) [AIBN] = 9.08×10^{-5} mol dm^{-3}, were 25 900 and 1.83 at 7% conversion and 20 400 and 2.56 at essentially complete, 100% conversion. When the initiator concentration was increased 20-fold, the values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ for the above-mentioned copolymer were 10 800 and 2.30 at 8% conversion. In the presence of constant initiator concentration, the gradual increase in the ratio of M_1:M_2 (from 7:93 to 92:8) was accompanied by a decrease in molecular weights ($\bar{M}_w$ from 46 430 to 21 570) and an increase in $\bar{M}_w/\bar{M}_n$ (from 1.74 to 2.14, respectively). These findings indicate that an increase in polymer radical combination occurs as the mole fraction of M_2 in the monomer feed increases.

Introduction

Incorporation of activated acrylates or methacrylates into polymers provides one of the most versatile routes for the preparation of reactive polymers. Copolymers of activated (meth)acrylates have, for example, been employed to study kinetic aspects of macromolecular reactions,[1] preparation of macromolecular drug carriers,[2] immobilized enzymes,[3] and polymeric reagents for peptide synthesis[4a] and transition-metal catalysis.[4b] A flexibly cross-linked equimolar copolymer[5] of 2,4,5-trichlorophenyl acrylate (M_1) and styrene (M_2) has, in particular, been found ideally suitable for the preparation of a wide range of polymeric reagents and polymer supports.[4,6] Currently, we are interested in the use of linear (soluble) copolymers of M_1 and M_2 for the development of electroreactive polymers suitable for the preparation of surface-modified electrodes and electrocatalysis. Systematic studies of the copolymerization of activated (meth)acrylates have, however, not been reported in the literature, and the data of ref 2 appear to represent the only previously published information. The present report describes the free radical copolymerization of M_1 and M_2 and the evaluation of the reactivity ratios by the Kelen and Tudos method.[7] A brief analysis of ^{13}C NMR spectra, the molecular weights ($\bar{M}_w$ and $\bar{M}_n$), and the polydispersity indices ($\bar{M}_w/\bar{M}_n$) of the copolymers is also presented.

Experimental Section

Materials. 2,4,5-Trichlorophenyl acrylate was prepared as described in the literature.[2] Styrene (Aldrich) was washed with 5% sodium hydroxide and distilled under reduced pressure. AIBN (BDH) was recrystalized from chloroform. Methanol and chlorobenzene (Rose Chemicals) were used as received.

Polymerization. The calculated amounts of M_1, M_2, AIBN, and chlorobenzene (see Table I) were placed in a standard Quickfit flask, and the mixture was flushed with nitrogen for 10 min. The flask was then tightly stoppered and maintained in a water bath at 60 ± 1 °C, and the polymerization was allowed to proceed to about 10% conversion (~30–70 min).

The reaction mixture was then poured into excess methanol, and the polymer was filtered, washed with methanol, and dried under vacuum at room temperature.

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Table I
Copolymerization[a] of 2,4,5-Trichlorophenyl Acrylate (M_1) with Styrene (M_2)

mole fraction of M_2 in feed	conversion,[b] wt %	Cl in polymer,[c] wt %	mole fraction of M_2 in copolymer (m_2)	GPC	
				$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0.0000	3.50	42.70	0.0000	20 357	2.00
0.0717	8.80	38.84	0.1766	21 573	2.14
0.1685	10.44	35.00	0.3346	22 700	1.99
0.2478	10.30	34.39	0.3568	20 920	2.08
0.3340	9.01	31.00	0.4679	22 970	1.78
0.5015	6.84	29.23	0.5190	25 940	1.83
0.6680	8.17	27.20	0.5726	34 260	1.70
0.7506	9.63	24.01	0.6478	30 470	1.83
0.8003	8.76	22.80	0.6737	30 690	1.87
0.8340	9.01	21.59	0.6983	40 990	1.66
0.9252	12.33	15.09	0.8132	46 430	1.74
1.0000	4.24		1.0000	43 686	1.69

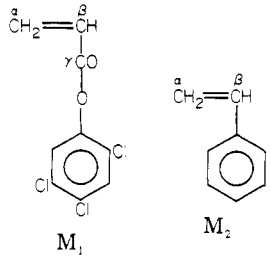
[a] $[M_1] + [M_2] = 0.81$ mol dm^{-3} in chlorobenzene in the presence of [AIBN] = 9.08×10^{-5} mol dm^{-3}. [b] 1-2% polymer was generally lost during precipitation. [c] Average of at least two determinations with an accuracy of better than ±1%.

Molecular Weight Determination. The weight-average molecular weights ($\bar{M}_w$) and the number-average molecular weights ($\bar{M}_n$) were determined by gel permeation chromatography (GPC). Tetrahydrofuran, stabilized with 2,6-di-*tert*-butyl-*p*-cresol, was used as eluent at a flow rate of 1 cm^3 min^{-1}. Polystyrene standards were used as calibration standards. (The molecular weights are not corrected for peak broadening and for the variation of refractive index with molecular weight.)

^{13}C NMR Spectroscopy: ^{13}C NMR spectra were recorded on a WH-250 spectrometer operating at 62.9 MHz in the pulsed Fourier transform mode, with decoupling from protons by broad-band irradiation. The free induction decays were recorded at 16K, and the chemical shifts (δ) were measured directly relative to Me_4Si.

Results and Discussion

Copolymerization of 2,4,5-trichlorophenyl acrylate (M_1) with styrene (M_2) was carried out at 60 °C in the presence



M_1

M_2

of AIBN as initiator and chlorobenzene as a solvent. Ten copolymer samples were prepared from feed ratios of M_1:M_2 = 8:92 to 93:7, and the copolymers were characterized by microanalysis, gel permeation chromatography (GPC), and ^{13}C NMR spectroscopy.

Reactivity Ratios. The reactivity ratios in the copolymerization of styrene with various (meth)acrylates, using IR[8] and NMR[9] spectroscopy, thin-layer chromatography,[10] light scattering,[11] and elemental analysis,[12] have been described. The reactivity ratios of a number of activated (meth)acrylates with several other monomers have been previously reported using elemental analysis.[2] For preliminary studies[13] we employed the carbonyl chromophore of M_1 to estimate the copolymer composition by IR (~1760 cm^{-1}) or UV (~280 nm) spectroscopy. Presently, however, chlorine analyses of the copolymers were found to be more convenient.

An average of at least two microanalyses was used for each copolymer, and the reproducibility of the results was found to be within ±1%.

A plot of copolymer composition vs. feed composition is shown in Figure 1. The reactivity ratios r_1 and r_2 of M_1 and M_2, respectively, were computed by a simple graphical

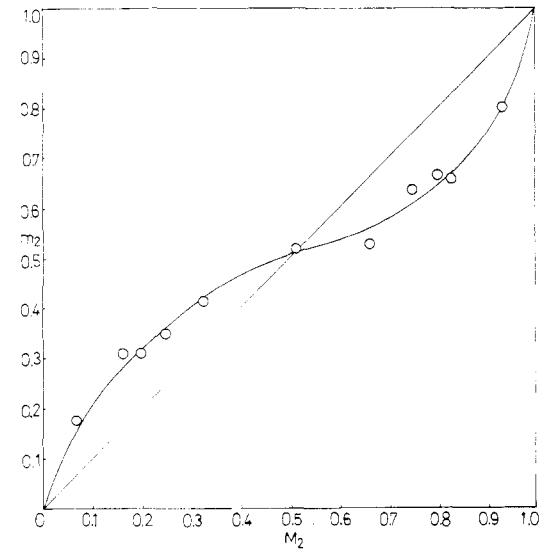


Figure 1. Mole fraction of styrene in copolymer (m_2) vs. mole fraction of styrene (M_2) in the feed.

method, namely, by using eq 1, proposed by Kelen and Tudos:[7]

$$\eta = \{r_1 + (r_2/\alpha)\}\xi - (r_2/\alpha) \quad (1)$$

where η and ξ are functions involving the composition of monomer feed and copolymer composition defined by Kelen and Tudos. A plot of η against ξ in eq 1 produces a straight line with $r_1 + (r_2/\alpha)$ as its slope and $-(r_2/\alpha)$ as its intercept. The choice of α depends on the distribution of the data along the η and ξ axes.

In general, Kelen and Tudos suggest[7] that $\alpha = (F_{max}F_{min})^{1/2}$ should be employed to maximize the symmetry of the data. For the present work, however, $(F_{max}F_{min})^{1/2} = 1.01$ and $\alpha = 1$ was found highly satisfactory, where F_{max} and F_{min} represent the highest and the lowest values of F measured for a given series of copolymers.

The values of x, y, F, G, η, and ξ (Kelen and Tudos parameters) are given in Table II. The parameters were also calculated by reindexing of the monomers, but the corresponding data are not presented in tabular form. Both sets of data are plotted in Figure 2, and, as expected,[7] both yield identical reactivity ratios of $r_1 = 0.29 \pm 0.03$ and $r_2 = 0.25 \pm 0.03$.

The relatively small value of $r_1r_2 = 0.073$ clearly indicates that M_1 and M_2 show a strong tendency for alternation in the copolymer (e.g., ref 17). This tendency toward alternation is probably related to the strongly electron-with-

Table II
Kelen and Tudos Parameters[a,b]

x	y	G	F	η[c]	ξ[c]
0.0808	0.2297	−0.2710	0.0284	−0.2635	0.0276
0.1990	0.4320	−0.2616	0.0917	−0.2396	0.0840
0.2495	0.4843	−0.2656	0.1286	−0.2353	0.1139
0.3323	0.5437	−0.2789	0.2031	−0.2318	0.1688
0.4970	0.7464	−0.1688	0.3309	−0.1268	0.2487
0.9940	0.9268	−0.0785	1.066	−0.0380	0.5160
1.994	1.137	0.2403	3.497	0.0535	0.7776
3.035	1.802	1.352	5.112	0.2212	0.8364
4.935	1.988	2.453	12.250	0.1851	0.9245
12.947	4.659	10.168	35.978	0.2750	0.9730

[a] Normal indexation of monomers. See text for details. [b] M_1 = 2,4,5-trichlorophenyl acrylate; M_2 = styrene. [c] α = 1.

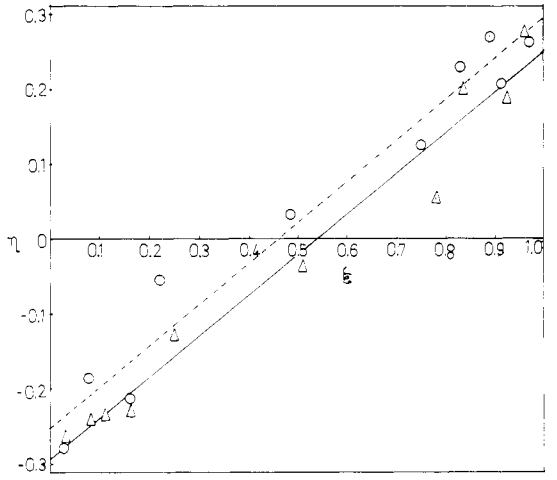


Figure 2. Estimation of reactivity ratios of M_1 and M_2 by the Kelen and Tudos method: (△) 2,4,5-trichlorophenyl acrylate = M_1, styrene = M_2; (○) reindexation of monomers (i.e., styrene = M_1, 2,4,5-trichlorophenyl acrylate = M_2).

drawing effects of the trichlorophenoxyl group in M_1 as compared with the phenyl group in M_2. Q and e values of M_1 were calculated from eq 2 and 3[17] to obtain Q_1 = 1.09 and e_1 = 0.82 (Q_2 = 1.0 and e_2 = −0.8 from standard references).

$$r_1 r_2 = \exp[-(e_1 - e_2)^2] \quad (2)$$

$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] \quad (3)$$

The presently reported Q_1 and e_1 values for 2,4,5-trichlorophenyl acrylate are somewhat different from the corresponding values reported previously for this monomer (Q_1 = 0.38 and e_1 = 0.59).[2] This may be explained, in part, by the general recognition that eq 2 and 3 do not provide a quantitatively accurate relationship between the reactivity ratios and Q–e values. Furthermore, it should be noted that the literature data[2] are based on copolymerization of M_1 with acrylamide (M_3). Routine observations suggest that controlled copolymerization of the strongly hydrophobic M_1 with a strongly hydrophilic monomer such as M_3 may be problematic due to the extremely different solubilities of the monomers (and the possibility of partial exclusion of the minor monomer from the vicinity of the propagating radicals).[14]

Molecular Weights. The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights and the polydispersity indices ($\bar{M}_w/\bar{M}_n$) of the copolymers are given in Table I. The mole fraction of M_2 in the corresponding feed mixtures and the resulting copolymers is also given in the same table. The most interesting result is that the gradual increase in the mole fraction of M_2 in the monomer mixture is accompanied by an increase in molecular weights and a decrease in $\bar{M}_w/\bar{M}_n$. A plot of $\bar{M}_w$ against the mole fraction of M_2 in the polymerization mixture is shown in Figure 3 and appears to be progressively curved as M_2 increases.

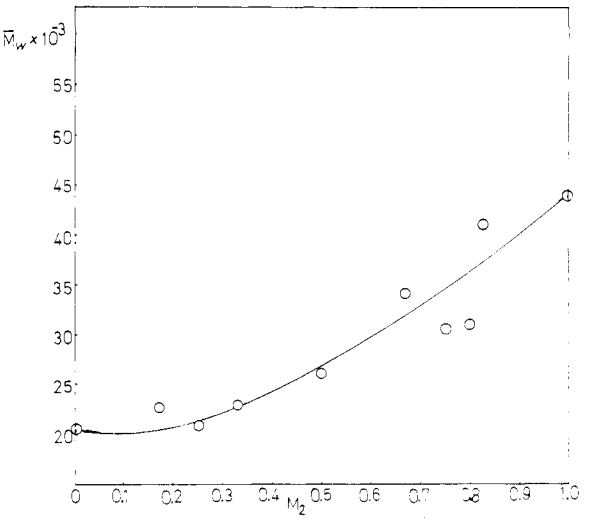
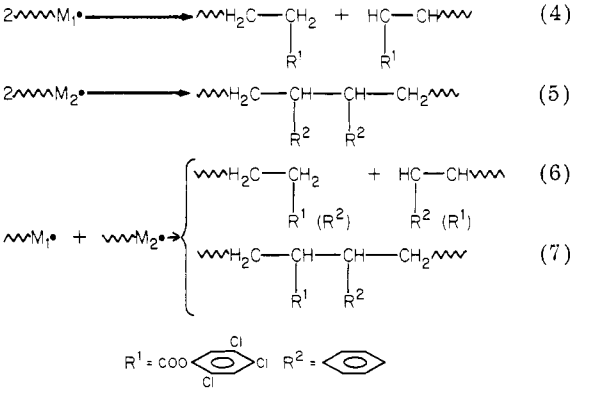


Figure 3. Dependence of $\bar{M}_w$ on the mole fraction of styrene (M_2) in the polymerization mixture.

It is known[12] that in the homopolymerization of styrene, the polymeric radicals (i.e., ~~M_2·) undergo termination, mainly by recombination. Poly(2,4,5-trichlorophenyl acrylate) radicals (i.e., ~~M_1·) are expected to terminate predominantly by disproportionation, as is the case for many (meth)acrylates.[15] The theoretical values of $\bar{M}_w/\bar{M}_n$ for polymer produced via radical recombination and radical disproportionation are 1.5 and 2.0, respectively.[15] The experimental values from the present work are 1.69 for poly(M_2), and 2.0 for poly(M_1) (see Table I), which are each in good agreement with the above-mentioned termination mechanisms, which are shown in eq 4 and 5.

The value of $\bar{M}_w/\bar{M}_n$ in copolymerization is also known to depend on the chain termination mechanisms in the same way as it does in the respective homopolymerizations.[16] The values of $\bar{M}_w/\bar{M}_n$ for various copolymers of M_1 and M_2 reported here (Table I) clearly suggest that there is an increasing tendency for combination of the polymer radicals involved in copolymerization to occur as the mole fraction of styrene in the monomer feed increases.



A further interesting feature of the copolymerization of M_1 and M_2 is the possibility of the rate of cross terminations being higher than the rate of the homoterminations. The importance of cross termination is usually expressed by the value of ϕ in eq 8, where k_{t11} and k_{t22} are the rate

$$\phi = k_{t12}/2(k_{t11}k_{t22})^{1/2} \quad (8)$$

Table III
^{13}C NMR Chemical Shifts of 2,4,5-Trichlorophenyl Acrylate (M_1) and Homo- and Copolymers of M_1 with Styrene (M_2)

compd	chemical shifts, ppm								
	C^1	C^2	C^3	C^4	C^5	C^6	C^α	C^β	C^γ
M_1	145.84	126.24	126.63	130.58	130.50	131.06	134.01	131.06	162.77
poly(M_1)[b]	145.19	125.68	131.03	131.68[a]	131.88[a]	125.16	34.77		171.15
			131.24					41.41	
	(155.3)	(121.4)	(131.9)	(129.1)	(134.5)	(118.8)	35.94		171.42
	145.26								
poly(M_2)	145.34	127.67[a]	128.35[a]	125.48			44.03	40.52	
	145.64	127.94		125.63			44.32		
copoly(M_1-M_2)									
component M_1	145.37	125.84	130.57	131.40[a]	131.40[a]	125.23	38.53	41.43	171.47
	145.55	125.37	130.88				38.68		171.68
							38.94		172.22
component M_2	141.76	127.00[a]	128.57[a]	125.23				40.97	
	142.15	127.66	129.66				41.98		
	142.83								
	143.55								

[a] The difference between these two values are within the limits of theoretical predictions. [b] The values given in parentheses are calculated values based on the substitutional parameters in phenol (cf.: Levy, G. C.; and Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; p 81).

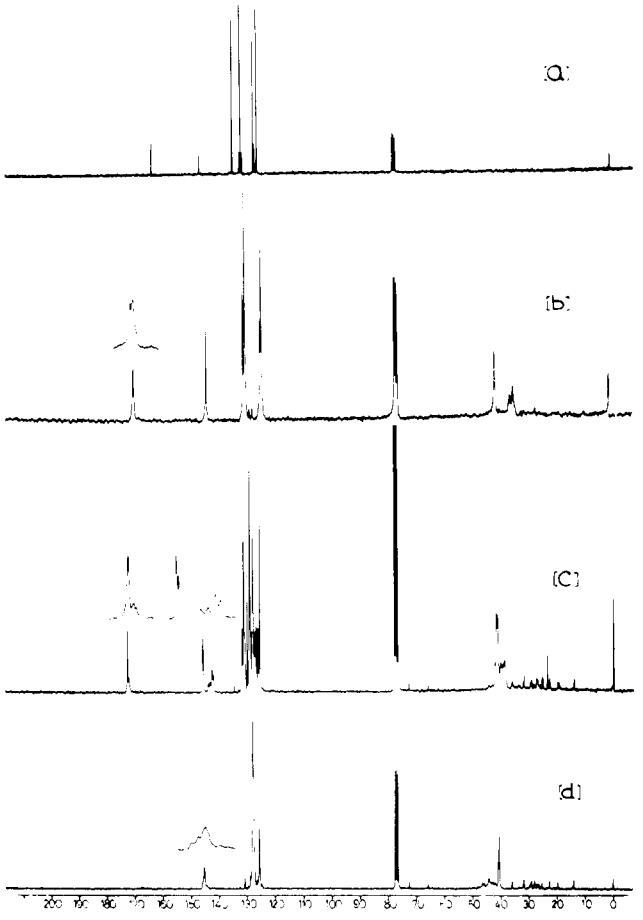


Figure 4. ^{13}C NMR spectra of (a) 2,4,5-trichlorophenyl acrylate (M_1), (b) poly(M_1), (c) copoly(M_1–50 mol % styrene), and (d) poly(M_2).

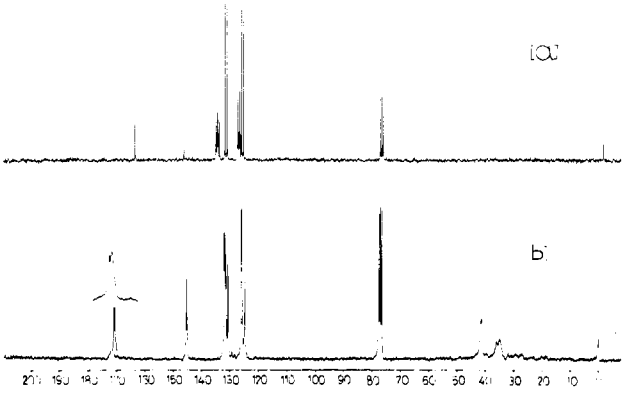


Figure 5. Off-resonance ^{1}H-decoupled ^{13}C NMR spectra of (a) 2,4,5-trichlorophenyl acrylate (M_1) and (b) poly(M_1).

constants for terminations between the like radicals[17] and k_{t12} is the rate constant for terminations between the unlike radicals.[17,18] When $r_1 \approx r_2$ and $\phi > 1$, then the rate of copolymerization decreases as the mole fraction of one of the monomers in the polymerization mixture increases and often passes through a minimum.[17,18] No detailed quantitative rate measurements of the copolymerizations listed in Table I were undertaken. However, it was observed that the relative rate of copolymerization decreased by a factor of 2–3 as the mole fraction of M_2 in the feed was increased from 0.07 to 0.5. This, together with the above discussion on the termination mechanisms of acrylate- or styrene-ended radicals suggested that $\phi > 1$ and that combination and disproportionation between unlike radicals was predominant and occurred as shown in eq 6 and 7.

It is noteworthy that $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ of the copolymer formed from an equimolar mixture of M_1 and M_2 were 20 400 and 2.56, respectively, at essentially complete conversion (≈16 h), as compared with the corresponding values of 25 900 and 1.83 at 7% conversion (25 min) (Table I). The interpretation of molecular weight data at high conversion is, however, generally difficult. In the present study, the molecular weights at high conversions are expected, apart from the gel effect, to be also influenced by various chain-transfer reactions.[15]

^{13}C NMR Spectroscopy. ^{13}C NMR spectra of 2,4,5-trichlorophenyl acrylate (M_1), its homopolymer, and its equimolar copolymer with styrene (M_2) are reported for the first time and are shown in Figure 4. The off-resonance ^{1}H-decoupled spectra of M_1 and poly(M_1) are given in Figure 5. Peaks due to carbon atoms attached to none, one, or two hydrogen atoms appear as a singlet, doublet, or triplet, respectively. Chemical shift assignments of various carbons are presented in Table III. It is interesting to note that all six of the carbon atoms of the phenyl ring in M_1 are clearly resolved due to substitutional effects of the chlorine atoms and the phenoxy carbonyl group.[19] In poly(M_1) (Figure 4b), the aromatic carbon C^1 is not split and appears as a singlet. This indicates that C^1 is away from the main chain and is not susceptible to tacticity,

whereas in poly(M_2) (see Figure 4d), C^1 is split into three peaks (with upfield intensities in the ratio 1:1.3:1.8), showing the presence of isotactic, heterotactic, and syndiotactic triads in the chain.[20] However, the carbonyl carbon (C^1) is susceptible to tacticity and is distinctly split into two peaks (relative upfield intensities in the ratio of 1:1.6). In copoly(M_1–M_2) (Figure 4c), C^1 of the M_1 units splits into two peaks (with relative upfield intensities of 1.5:1), whereas C^1 of the M_2 units is split into four peaks (with relative intensities, upfield, of 1:1.2:3.3:1.7). Similarly, the carbonyl carbon in the same copolymer is split into three peaks (relative upfield intensities of 10.2:2.3:1). The additional splittings in copoly(M_1–M_2) over those observed in the respective homopolymers indicate the presence of unsymmetrical sequence triads in the copolymer chains. A detailed study of the sequence distribution of M_1 and M_2 in the copolymers will be reported in the future.

A set of upfield peaks with low intensity (around 15–35 ppm) and also downfield peaks (at 65.84, 72.54, and 130.77 ppm) in the spectra of poly(M_2) (Figure 4d) and copoly(M_1–M_2) (Figure 4c) seem to be due to the end groups that are attached to the low molecular weight polymer chains. For reasonably high molecular weight polystyrene ($\bar{M}_n \simeq$ 80 000), the ^{13}C spectrum does not show any peaks in these regions. However, it is rather difficult to identify the chemical nature of end groups purely by ^{13}C NMR because of their low concentration.

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Registry No. 2,4,5-Trichlorophenyl acrylate, 40952-23-6; styrene, 100-42-5; 2,4,5-trichlorophenyl acrylate–styrene copolymer, 87555-24-6.

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Amphoteric Polymerization Behavior of 7,7,8,8-Tetrakis(ethoxycarbonyl)quinodimethane in Its Alternating Copolymerizations

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ABSTRACT: The preparation and polymerization behavior of 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ) were studied to confirm an amphoteric behavior in the charge-transfer complex formation and in the radical alternating copolymerization. Both of these amphoteric behaviors could be well explained in terms of the π-electron density scheme. TECQ was found to exhibit very poor homopolymerizability with radical, cationic, and anionic initiators relative to the moderate one for 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane.

Several electron-accepting quinodimethane compounds, namely, 7,7,8,8-tetracyanoquinodimethane (TCNQ),[1,2] 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$),[3] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane,[4] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[5] 2,5,7,7,8,8-hexacyanoquinodimethane,[6] 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP),[6] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ),[7] have been studied in their alternating copolymerization as acceptor monomers and their initiation ability for the cationic polymerization of vinyl ethers. Especially noticeable is an amphoteric behavior of TMCQ in its alternating copolymerizations; it acts as an acceptor monomer toward a donor monomer such as styrene (St), a vinyl ether, and vinyl acetate, while it is a donor monomer toward the very powerful electron-accepting mo-

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