consisting of polycarbonate and polyester chains is possible by taking advantage of the living nature of the copolymerizations.

References and Notes

(1) Recent reviews on alternating copolymerization: (a) Gaylord, N. G. *J. Polym. Sci., Part C* **1970**, *31*, 247. (b) Hirai, H. *Macromol. Rev.* **1976**, *11*, 47. (c) Hirooka, M. *Sekiyu Gakkaishi* **1977**, *20*, 1093. (d) Furukawa, J.; Kobayashi, E. *Rubber Chem. Technol.* **1978**, *51*, 600. (e) Saegusa, T. *Makromol. Chem., Suppl.* **1979**, *3*, 157.

(2) (a) Szwarc, M. "Carbanion, Living Polymers, and Electron-Transfer Processes"; Interscience: New York, 1968. (b) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1. (c) Webster, O. W.; Hertler, W.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. U. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (d) Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49. (e) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814.

(3) Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules* **1985**, *18*, 1049.

(4) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358.

(5) The copolymerization of phthalic anhydride and 1,2-epoxypropane (50 mmol/50 mmol) with the (TPP)AlOR (1, X = OR)-PPh_3 (1 mmol/2 mmol) system in CH_2Cl_2 (60 mL) at room temperature for 24 h gave the alternating copolymer in a quantitative yield: $\bar{M}_n$ = 3000, $\bar{M}_w/\bar{M}_n$ = 1.1. On the other hand, in the absence of PPh_3 under similar conditions for 1 month, the copolymer containing 53% ether linkages and 47% ester linkages ($\bar{M}_n$ = 5500, $\bar{M}_w/\bar{M}_n$ = 1.1) was formed with the complete consumption of epoxide (unpublished results).

(6) (a) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162. (b) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166.

(7) (a) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792. (b) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1984**, *17*, 2217.

(8) Inoue, S.; Aida, T. "Ring-Opening Polymerization"; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science: London, 1984; Vol. 1, p 242.

(9) (a) Inoue, S. *Prog. Polym. Sci. Jpn.* **1975**, *8*, 1. (b) Inoue, S., Yamazaki, N., Eds. "Organic and Bio-organic Chemistry of Carbon Dioxide"; Kodansha: Tokyo, 1981; p 167.

(10) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(11) Hoffmann, H.; Gruenewald, R.; Horner, L. *Chem. Ber.* **1960**, *93*, 861.

(12) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304.

(13) Aida, T.; Inoue, S. *Macromolecules* **1982**, *15*, 682.

(14) For $CH_2{=}CHP^+Ph_3Br^-$: δ 18.99 (P^+), ^{31}P NMR in $CDCl_3$; δ 117.5 ($J_{C(sp^2)-P^+}$ = 80.6 Hz) (CH), δ 143.7 (CH_2), $^{13}C\{^1H\}$ NMR in $CDCl_3$. Eusley, J., Hall, D., Ed., "The Chemistry of Phosphorus"; Harper and Row: London, 1976; p 77.

(15) Schweizer, E.; Bach, R. *J. Org. Chem.* **1964**, *29*, 1746.

Thermally Depolymerizable Polycarbonates. 2. Synthesis of Novel Linear Tertiary Copolycarbonates by Phase-Transfer Catalysis

F. M. Houlihan, F. Bouchard, and J. M. J. Fréchet*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

C. G. Willson

IBM Research Laboratory, San Jose, California 95193.
 Received April 18, 1985

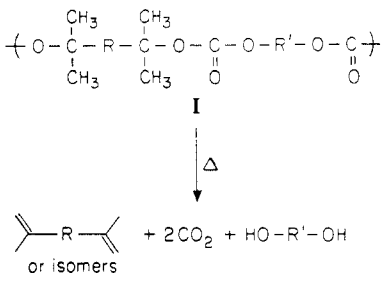
ABSTRACT: The first synthesis of copolycarbonates containing a tertiary diol structure has been achieved by using a solid–liquid phase-transfer-catalyzed polycondensation of the bis(carbonylimidazolide) of 2,5-dimethyl-2,5-hexanediol with various other diols in the presence of powdered potassium carbonate. The solubility and physical properties of the copolycarbonates are affected by the nature of the diol used in the polycondensation. Higher melting polymers are obtained when the diol structure incorporates an aromatic ring while increased solubility results from increased steric crowding or the incorporation of less symmetrical or aliphatic structures in the diol component. The copolycarbonates decompose cleanly upon heating to approximately 200 °C with liberation of volatile materials, leaving no solid residue. For example, the copolycarbonate of 2,5-dimethyl-2,5-hexanediol and *p*-benzenedimethanol is stable to 200 °C, and then undergoes rapid thermolysis with formation of carbon dioxide, *p*-benzenedimethanol, and a mixture of three dienes corresponding to all the possible dehydration products of 2,5-dimethyl-2,5-hexanediol. The thermal lability of the polycarbonates allows their analysis by gas chromatography–mass spectroscopy using direct solid sample injection.

Introduction

The synthesis of novel polymeric materials that can be modified by physical processes such as heating, irradiation, and/or changes in pressure is of great interest as these materials are finding numerous applications as coatings, additives for postreaction within preformed polymers, cross-linking agents, blowing agents, adhesives, etc. We have recently described the synthesis of poly[*p*-((*tert*-butyloxycarbonyl)oxy)styrene][2] and its α-methylstyrene analogue[3] as useful polymeric precursors to the corresponding poly(*p*-hydroxystyrene) and poly(*p*-hydroxy-α-methylstyrene). The *tert*-butyloxycarbonyl (t-Boc) protecting group was chosen for these syntheses, as it afforded stable yet easily removable protection for the phenolic groups of *p*-hydroxystyrene while allowing for easy and controlled polymerization. Although the t-Boc protecting group has been used mainly for the protection of amino groups in applications such as the synthesis of polypeptides,[4] we have demonstrated recently[5] its general applicability to the protection of alcohol, phenol, enol, and thiol functionalities. The t-Boc group is particularly interesting in these applications, as it can be removed under mild conditions.[4,6,7] Several polymers containing thiol pendant groups have been prepared by thermolysis of solutions of their thiocarbonate derivatives.[8] In the case of t-Boc-protected phenolic polymers,[1,2] we have found that removal of the protecting groups is best achieved[1] by heating the polymers, in the solid state, to approximately 190 °C. When followed thermogravimetrically, the deprotection reaction is characterized by no measurable loss of mass until the critical temperature is reached, whereupon virtually instantaneous and quantitative loss of the elements of the t-Boc protecting group (carbon dioxide and 2-methylpropene) is observed. The thermal deprotection

0024-9297/86/2219-0013$01.50/0

Scheme I



procedure is remarkable in that it affords a phenolic polymer that is of a purity difficult to obtain by any other route, and it does not affect the degree of polymerization of the polymer, in sharp contrast with the behavior of other thermally labile polymers.

The clean thermal degradation of phenolic *tert*-butyloxy carbonates suggests that polymers containing similar carbonate groups in their main chain should afford a new class of potentially useful thermally depolarizable materials. This report describes our approach toward the design of such linear tertiary copolycarbonates and the synthesis and thermal characteristics of such polymers.

Results and Discussion

The removal of *tert*-butyloxycarbonyl protecting groups from amines by acidolysis is a reaction that has been well documented in the pioneering work of Carpino and others.[6] In contrast, the thermolysis reaction[7] has received little attention, as it is less readily applicable to peptide synthesis.

If one considers the removal of the t-Boc group from a compound such as the *tert*-butyloxycarbonyl derivative of 3,5-dimethylphenol, the thermolysis reaction affords carbon dioxide and 2-methylpropene in addition to the parent 3,5-dimethylphenol. As this reaction is susceptible to acid catalysis, it can be assumed that the reaction proceeds by homolytic or heterolytic cleavage of the C–O bond adjacent to the *tert*-butyl group to afford a relatively stable tertiary intermediate which, in turn, decomposes to the observed 2-methylpropene.

If this mechanism is indeed operative, a thermally degradable polymer should result from the incorporation of tertiary diol moieties in a polycarbonate structure. Tertiary polycarbonates such as I (Scheme I) are expected to be unique in their thermolytic behavior, showing complete stability below the critical decomposition temperature, but exhibiting a near-instantaneous and quantitative decomposition into volatile low molecular weight compounds above the critical decomposition temperature. Many other polymers are known to undergo a thermal decomposition when heated above their ceiling temperature but these materials, as typified by α-methylstyrene, frequently undergo depolymerization in a slow, stepwise process proceeding from the chain ends. This behavior is to be contrasted with the proposed tertiary polycarbonates such as I, which suffer multiple, simultaneous main-chain cleavage reactions and are therefore degraded extremely rapidly in a process that, unlike the ceiling temperature phenomenon, is irreversible.

Preparation of the Tertiary Polycarbonates. The synthesis of polycarbonates of tertiary diols is not reported in the literature as these polymers are difficult to make due to the lack of stability of the chloroformates of tertiary alcohols.[9] Even the chloroformate of *tert*-butyl alcohol is known to be unstable[10] and is of little use in the preparation of *tert*-butyloxy carbonates. Similarly, the reaction of a bifunctional chloroformate with a bis(tertiary diol) is not expected to be suitable for the preparation of a polymer due to the low reactivity of the tertiary diols. Our search for a stable yet reactive substitute for the tertiary chloroformate moiety led us to consider the tertiary carbonylimidazolide group which has been reported by Staab.[11]

Thus Staab describes the reaction of the phosgene analogue, carbonyldiimidazole, with *tert*-butyl alcohol in the presence of a small amount of *tert*-butoxide to yield (*tert*-butylcarbonyl)imidazole as a white crystalline material which is thermally and hydrolytically stable. Further reaction of this compound with *tert*-butyl alcohol in the presence of *tert*-butoxide affords the symmetrical *tert*-butyl carbonate in good yield.[11] This reaction, which appears promising for the synthesis of a linear tertiary polycarbonate using a tertiary diol and carbonyldiimidazole, was tested with 2,5-dimethyl-2,5-hexanediol. This choice of diol was dictated by the need to avoid the possible competing ring-closure side reaction which would result in the formation of a five- or six-membered ring internal carbonate if either a 1,2- or 1,3-diol were used in the reaction. Indeed, such cyclizations are reported to occur when simple 1,2-diols are treated with 1,1′-thiocarbonyldiimidazole[12] and our own model studies have confirmed that pinacol forms a five-membered-ring carbonate in essentially quantitative yield by reaction with the carbonylimidazolide of benzyl alcohol.[13] The bis(carbonylimidazolide) III of 2,5-dimethyl-2,5-hexanediol was prepared successfully (Scheme II) as a white crystalline material that is relatively stable but is susceptible to a slow thermolysis reaction (IV) when stored at or above room temperature for extended periods of time. Upon treatment with a variety of simple diols V under base catalysis, the bis(carbonylimidazolide) III affords the expected linear tertiary copolycarbonates VI (Table I). The reaction is best carried out under phase-transfer catalysis using powdered anhydrous potassium carbonate and 18-crown-6. Satisfactory results can also be obtained by using simple alkoxides but the reaction under phase-transfer conditions affords the best results. In general, the phase-transfer reaction proceeds best in dichloromethane. Fully tertiary polycarbonates can be obtained by reaction in this solvent. Oligomeric tertiary carbonates are obtained if the reaction is run in THF.

In view of the relative basicities of alcohols, phenol, and imidazole, the reaction is only applicable to the preparation of copolycarbonates from tertiary diols and other diols but not to a similar reaction with bisphenols, as the phenolate group is a better leaving group than imidazolide. Formation of a homopolymer containing only 2,5-dimethyl-2,5-hexanediol units (VIa) is possible but the reaction is sluggish; only oligomeric carbonates are obtained. The product of the reaction of III with Va is a tacky material that still shows a strong OH band in the infrared along with the expected C=O and C—O—C bands. It is likely that the steric crowding of both III and Va is responsible for this incomplete condensation reaction. In contrast, both primary and secondary diols can be used in the polycondensation with III to afford good yields of a variety of copolycarbonates VIb–f (Table I). For example, the reaction of *p*-benzenedimethanol (Vb) with bis(carbonylimidazolide) III gives a white powdery polycarbonate (VIb) in 80% yield. The polymer shows no hydroxyl band in its infrared spectrum and has large carbonyl and C—O—C bands at 1739 and 1162 cm^{-1}, respectively. Polymer VIb is soluble in chlorinated solvents and melts near 140 °C, as shown by DSC. Thermogravimetric analysis of VIb confirms that it undergoes complete depolymerization near

Scheme II

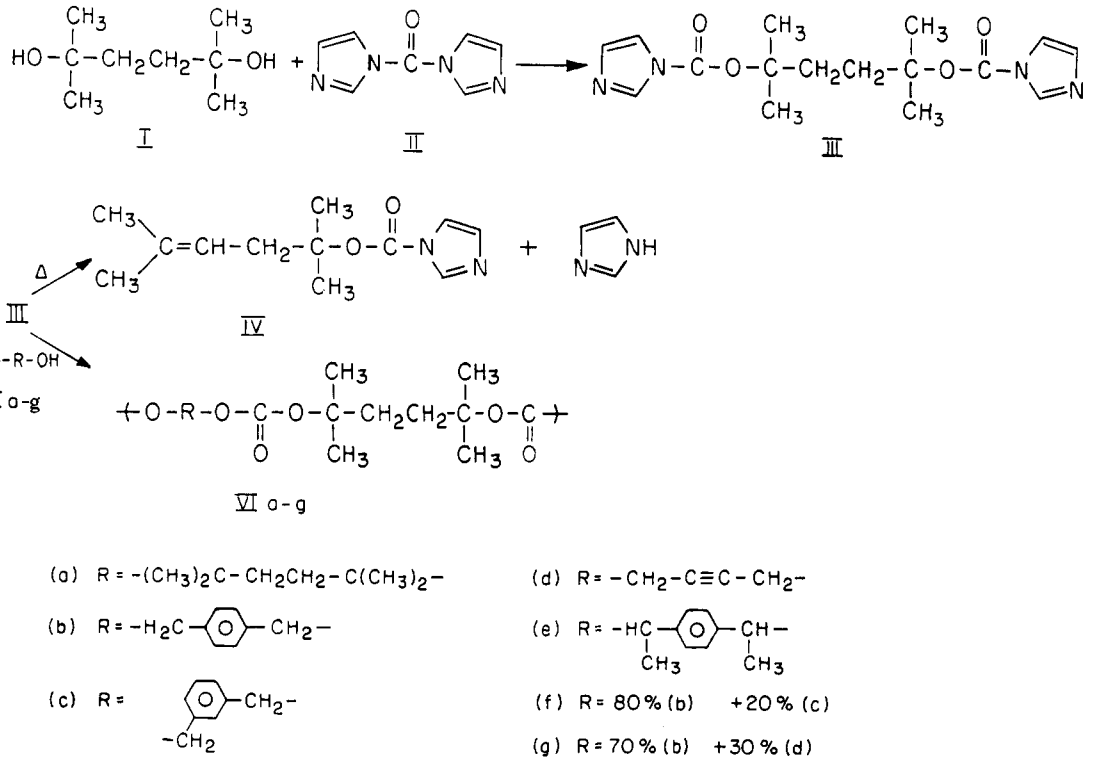


Table I
Preparation of the Copolycarbonates from 2,5-Dimethyl-*O*,*O*'-bis(1-imidazoylcarbonyl)-2,5-hexanediol

polymer	structure	reacn time,[a] h	reacn yield, %	polymer anal. C, H found (calcd)	mp,[b] °C	M_n(osm)[c] (M_n(end group))[g]	M_n(GPC[d])	M_w(GPC[d])	M_w/M_n-(GPC)
VIa	2,5-dimethyl 2,5-hexanediol	48	71		*e*				
VIb	1,4-benzenedimethanol	12	80	64.13, 7.23 (64.27, 7.19)	150	7.2×10^3 (6.6×10^3)	*f*		
VIc	1,3-benzenedimethanol	12	64	64.54, 7.43 (64.27, 7.19)	*e*	(37×10^3)	13.8×10^3	21.8×10^3	1.6
VId	1,4-butynediol	12	70	58.97 7.08 (59.17, 7.19)	*e*	(10.8×10^3)	11.1×10^3	15.7×10^3	1.5
VIe	*p*-bis(1-hydroxyethyl)benzene	12	71	66.19, 7.98 (65.91, 7.74)	93	10.3×10^3 (7.3×10^3)	17.8×10^3	3.07×10^3	1.7
VIf	80% 1,4- + 20% 1,3-benzenedimethanol	12	84	64.42, 7.28 (64.27, 7.19)	125	9.9×10^3 (10.2×10^3)	14.8×10^3	22.9×10^3	1.5
VIg	80% 1,4-benzenedimethanol + 20% 1,4-butynediol	12	77		128	(13.7×10^3)	6.8×10^3	12.9×10^3	1.9
VIg	70% 1,4-benzenedimethanol + 30% 1,4-butynediol	24	80	63.27, 6.97	115	(17.6×10^3)	7.1×10^3	13.4×10^3	1.9

[a] Reaction with K_2CO_3/18-crown-6 solid–liquid phase transfer in refluxing CH_2Cl_2 or THF. [b] Measured by DSC. [c] In 1,2-dichloroethane. [d] In THF with column calibrated for styrene. [e] Polymer is tacky at room temperature. [f] Polymer is insoluble in THF. [g] Calculated values assuming tertiary diol end units.

200 °C. as expected, this temperature is very close to that necessary for the thermal removal of the t-Boc groups of poly[*p*-((*tert*-butyloxycarbonyl)oxy)styrene]. In addition, the shape of the TGA curve is characteristic of a rapid process such as that observed in the thermolysis of the t-Boc group of poly[*p*-((*tert*-butyloxycarbonyl)oxy)-styrene].

The effect of the structure of diol V on the properties of the final copolycarbonate VI was studied with the aim of preparing a copolymer with solubility in a wide variety of solvents and a relatively high melting temperature. One way to increase the solubility of a polymer is to decrease the symmetry of the chains, thus hindering close packing of the chains and lowering the crystallinity of the polymer. For example, replacing *p*-benzenedimethanol (Vb) by its meta isomer (Vc) results in the formation of a copolymer that is soluble in a wide variety of solvents but is a soft material with poor mechanical properties. A simple modification of the copolymerization conditions involving the use of a 4:1 mixture of Vb and Vc resulted in the formation of a solid polymer VIf (Table I) with improved solubility and mechanical properties (as compared to VIb). A thermogravimetric analysis of VIf gave results that were essentially identical with those obtained for VIb with onset of the rapid decomposition of the polymer near 200 °C while a DSC study showed multiple endotherms at 68, 101, and 125 °C, likely corresponding to thermal transitions of metastable crystalline forms of the polymer. Repeated measurements of the DSC curve after initial heating to 140 °C showed only one endotherm at 125 °C.

The fully aliphatic copolymer VId obtained by reacting the bis(carbonylimidazolide) III with 2-butyne-1,4-diol is

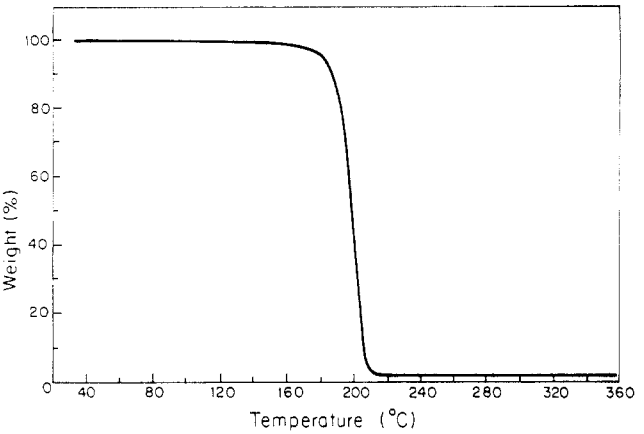


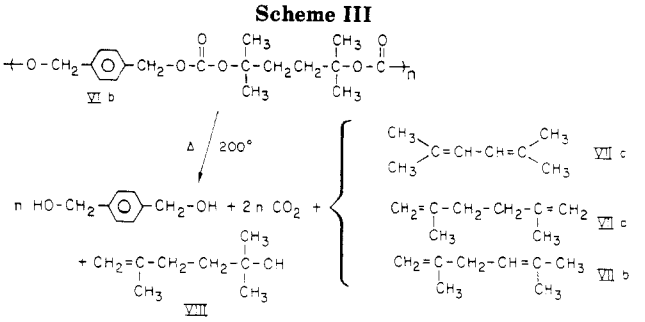
Figure 1. TGA of polycarbonate VIg obtained by condensation of 80% 1,4-benzenedimethanol and 20% 1,4-butynediol with 2,5-dimethyl-*O*,*O*′-bis(1-imidazoylcarbonyl)-2,5-hexanediol.

obtained as a soft material with poor mechanical properties that decomposes sharply near 190 °C as measured by TGA. Since the presence of a linear, alkyne structure in the backbone of VId was expected to afford close packing of the polymer chains, this finding indicates that the interchain interactions associated with the presence of aromatic rings, as in the case of VIb, are important in the design of higher melting copolycarbonates with structure VI. Again, this is confirmed by the preparation of polymer VIg; this polymer, which is obtained by condensation of III with a mixture of 80% 1,4-benzenedimethanol and 20% 1,4-butynediol, melts at 128 °C. The thermogravimetric trace obtained for VIg (Figure 1) shows that the polymer undergoes complete and essentially instantaneous depolymerization when heated near 190 °C as is the case with all other polycarbonates containing the tertiary diol structure I.

Finally, condensation of bis(carbonylimidazolide) III with a secondary diol such as 1,4-bis(1-hydroxyethyl)-benzene affords a good yield of the copolycarbonate VIe (Table I). This polymer having aromatic units in the backbone has a relatively high melting point (93 °C) as determined by DSC and good solubility in a wide variety of organic solvents. The enhanced solubility of VIe as compared to VIb is likely due to the presence of the methyl groups on the benzylic positions, which, in turn, have an influence on the crystallinity of the polymer chains. The thermal depolymerization of VIe occurs as expected near 220 °C with evolution of carbon dioxide, leaving no solid residue.

Analysis of the Thermolysis Product. As polymers VIa–g are designed to undergo rapid and complete thermolysis to yield volatile materials only, much interesting information can be obtained by mass spectral analysis of the solid polymer or of its decomposition products following their separation by gas chromatography. For example, analysis of VIb by mass spectrometry confirms that the expected decomposition does indeed take place with CO_2 extrusion and liberation of *p*-benzenedimethanol and diene moieties derived from the parent 2,5-dimethyl-2,5-hexanediol as shown in Scheme III. More useful data can be obtained if the solid polymer samples are inserted into the injection port of a gas chromatograph, the outlet of which is coupled to the mass spectrometer. Under these conditions, all of the thermolysis products can be seen individually and identified. With all polycarbonates derived from 2,5-dimethyl-2,5-hexanediol, the three possible diene dehydration products of I, namely, 2,5-dimethyl-1,5-hexadiene (VIIa), 2,5-dimethyl-1,4-hexadiene (VIIb), and 2,5-dimethyl-2,4-hexadiene (VIIc), are obtained in

Scheme III



varying amounts, with the first two predominating. The conjugated diene VIIc is only obtained in 9–15% yield, indicating that the thermolysis reaction is kinetically controlled.

Although, polymers VIa–g are obtained from bis(carbonylimidazolide) III, and thus imidazole residues can be expected at the end of some polycarbonate chains, no imidazole can be detected by GC–MS of VIa–g.

This finding is not unexpected as the carbonylimidazolide groups that might be located at the ends of some chains when the polymerization is stopped are likely cleaved during workup and are replaced by hydroxyl groups in the isolated polymer. This is confirmed by the presence of small amounts of an unsaturated alcohol, 2,4-dimethyl-hex-5-en-2-ol (VIII) or its 4-unsaturated isomer, in the thermolysis product of VIb–g.

Characterization of the alcohol fragments originating from thermolysis of VIa–g was facilitated by experiments in which samples of the polycarbonates were brought to their decomposition temperatures in sealed tubes and then treated with a silylating agent prior to GC–MS analysis; in all cases M^+ peaks were observed for the silylated alcohol products. Results of the GC–MS analysis for the various thermolysis reactions are given in Table II. Some interesting data can be obtained by evaluation of the ratio of unsaturated alcohol VIII to the total amount of species derived from 2,5-dimethyl-2,5-hexanediol, namely, compounds VIIa–c and VIII. Since VIII originates from chain ends only, this ratio is directly related to the number-average molecular weight of the polycarbonates. Statistical considerations would suggest that, on average, for polymers VIb–g, one end of each polycarbonate chain is derived from a tertiary diol unit while the other end is derived from the other diol component. In the case of VIb (Table II), a typical experiment indicates that unsaturated alcohol VIII accounts for 7.9% of all products derived from 2,5-dimethyl-2,5-hexanediol. Assuming that VIII originates from one end group of polymer VIb only, the value of M_n would be 4.25×10^3, while a value of 8.5×10^3 would be obtained if both ends of polycarbonate VIb gave rise to VIII upon thermolysis. Osmometry measurements for VIb indicate a value of $M_n = 7.2 \times 10^3$, suggesting that indeed the tertiary diol moieties make up a majority of the polymer end groups. The values given in Table I for M_n, calculated by end-group analysis using GC–MS results, are reported assuming tertiary diol end units only.

With polycarbonate VIa, the amount of unsaturated alcohol VIII produced during thermolysis cannot be correlated to the molecular weight of the polymer as chain scissions occurring at any point of the polymer chain, and not only at the chain ends, can be responsible for the formation of VIII. In fact, the thermolysis of VIa only affords a small amount of dienes VIIa–c, and VIII is the major product of the reaction.

GC–MS analysis also afforded confirmation of the degree of incorporation of each diols in the final polymer with

Table II
Thermal Decomposition of the Copolycarbonates and GC–MS Analysis of the Thermolysis Products

polymer[a]	T(dec), °C	alcohol fragments	characteristic peaks m/e	diene fragments	characteristic peaks m/e
VIb	210	$HOCH_2C_6H_4CH_2OH$ para (major)	M^+ = 138 (m), 12 (w), 120 (w), 107 (vs), 92 (m), 91 (m), 79 (s), 77 (m)	$CH_2{=}C(CH_3)CH_2CH_2C(CH_3){=}CH_2$	M^+ = 100 (w), 95 (s), 81 (m), 77 (w), 68 (s), 57 (m), 55 (vs)
		$CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~10.1%)	M^+ (absent) 113 (vw), 10 (w), 95 (m), 70 (m), 59 (vs), 55 (m), 43 (s)	$CH_2{=}C(CH_3)CH{=}C(CH_3)_2$	M^+ = 100 (m), 95 (vs), 81 (w), 77 (w), 68 (w), 67 (m), 55 (m)
				$(CH_3)_2C{=}CH{-}CH{=}C(CH_3)_2$	M^+ 110 (s), 95 (vs), 81 (w), 77 (w), 68 (w), 67 (m), 55 (m)
				ratio ≃ 3.8:3.6:1	
VIc	195	$HOCH_2C_6H_4CH_2OH$ meta $CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~1.8%)	M^+ = 138 (s), 121 (w), 107 (s), 92 (m), 91 (s), 79 (vs), 77 (s)	as above for VIb, ratio ≃ 4.5:4.5:1	
VIf	200	$HOCH_2C_6H_4CH_2OH$ meta $HOCH_2C_6H_4CH_2OH$ para $CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~6.6%)	see VIc	as above for VIb, ratio ≃ 3.2:2.8:1	
VIe	220	$HO(CH_3)CHC_6H_4CH(CH_3)OH$ para	M^+ = 166 (w), 151 (vs), 148 (w), 133 (w), 30 (w), 21 (w), 105 (s), 91 (w), 19 (m), 77 (m)	as above for VIb, ratio ≃ 5:4.5:1	
		$CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~9.8%)			
VId	190	$HOCH_2C{\equiv}CCH_2OH$	M^+ = 86 (vw), 68 (w), 57 (vw), 55 (m), 39 (s)	as above for VIb, ratio ≃ 4.6:4.4:1	
		$CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~5.2%)			
VIg	190	$HOCH_2C_6H_4CH_2OH$ para	see VIb	as above for VIb, ratio ≃ 3.7:3.3:1	
		$HOCH_2C{\equiv}CCH_2OH$	see VId		
		$CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~4.7%)	see VIb		
VIa		$HO(CH_3)_2CCH_2CH_2C(CH_3)_2OH$	M^+ (absent) 113 (w), 10 (vw), 95 (w), 70 (s), 59 (vs), 55 (m), 43 (vs)	as above for VIb but very weak, ratio ≃ 6:4:1	
		$CH_2{=}C(CH_3)CH_2CH_2C(CH_3)_2OH$ (~70%)	see VIb		

[a] The thermolysis of the polymers is studied by using GC–mass spectra. [b] Depolymerization temperatures measured by TGA. [c] The number in parentheses represents the percent of unsaturated alcohol unit VIII in all products derived from 2,5-dimethyl-2,5-hexanediol. [d] The ratio of dienes is calculated from the GC after calibration with authentic samples.

the polycarbonates obtained by reaction of mixtures of nontertiary diols with III. In general, this was in close agreement with the composition of the diol mixture used in the polycondensation reaction.

Conclusion

The combination of phase-transfer catalysis with the use of bis(carbonylimidazolides) such as III as reactive species appears to be well suited for the preparation of otherwise inaccessible tertiary polycarbonates. This class of polycarbonates is unique in its ability of undergo multiple, simultaneous, main-chain cleavage reactions with the formation of volatile products only. This property allows for easy analysis of the polymers by GC–MS. The materials may find applications in thin-film technology due to their unique thermolytic behavior.

Experimental Section

1,1′-Carbonyldiimidazole (Sigma), *p*- and *m*-benzenedimethanol, and 2,5-dimethyl-2,5-hexanediol (Aldrich) were used without purification; 2-butyne-1,4-diol (Aldrich) was purified by chromatography while 1,4-bis(1-hydroxyethyl)benzene was prepared by $NaBH_4$ reduction of *p*-diacetylbenzene (Aldrich). All solvents used in reactions with 1,1′-carbonyldiimidazole or derivatives were dried prior to use.

Infrared spectra were measured on a Nicolet MX1 FT-IR as KBr pellets or liquid films on NaCl disks. NMR spectra were recorded on Varian EM-360, CFT 80, XL-200, or XL-300 instruments in $CDCl_3$, using Me_4Si as the internal standard. Mass spectra were taken with a VG-7070E double-focusing mass spectrometer either using the normal thermal probe or using chemical ionization with methanol. In the analysis of polymers VIa–g, a solid sampling device was used in combination with the GC–MS analysis system. The columns used for separation of the thermolysis products were 30-m capillary columns packed with 6% OV-17 on Chromosorb-W/HP, 100–200 mesh. Calibration of the gas chromatographic peaks was accomplished by using authentic samples. Molecular weight determinations for polymers were done either by comparison with polystyrene standards using a Waters Model 150 gel permeation chromatograph equipped with a series of five μ-Styragel columns of different exclusion volumes and tetrahydrofuran as the mobile phase or by using a Wescan Model 231 recording membrane osometer with 1,2-dichloroethane as the solvent. Thermogravimetric analysis (TGA) and differential scanning calorimetry were done using a Du Pont 1090 instrument at a heating rate of 10 °C/min under a nitrogen atmosphere.

(1) Synthesis of the Bis(carbonylimidazolide) of 2,5-Dimethyl-2,5-hexanediol (III). A solution of 40.0 g (0.274 mol) of 2,5-dimethyl-2,5-hexanediol dissolved in 400 mL of dry THF was treated with 1 g of potassium metal under an argon atmosphere. The reaction mixture was then refluxed until all the potassium metal dissolved. The temperature was then lowered to 30 °C, and the solution was transferred, under argon, to a flask containing a stirred suspension of 88.6 g (0.547 mol) of 1,1′-carbonyldiimidazole in 200 mL of dry THF. After complete addition, the stirred reaction mixture was heated to 65 °C for 1 h, after which time monitoring indicated that the reaction was complete. The workup was done by adding ethyl acetate to the reaction mixture and washing the resultant solution several times with distilled water. The washed organic layer was dried over anhydrous magnesium sulfate and then evaporated to yield the crude product. Purification by liquid chromatography on silica gel, using ethyl acetate as an eluent, afforded 65.0 g (71.0% yield) of a white crystalline solid with a melting point of 94–96 °C. This

Table III
Spectroscopic Properties of the Copolycarbonates

polymer	IR, cm^{-1}	^1H NMR, ppm from $CDCl_3$	^{13}C NMR, ppm from $CDCl_3$
VIa	3439, 1736, 1473, 1455, 1377, 1297, 1260, 1214, 1160, 1130, 1094, 1052, 1003	1.40 (s, 12 H), 1.75 (m, 4 H)	
VIb	1738, 1519, 1477, 1454, 1386, 1371, 1259, 1203, 1160, 1085, 869, 793	1.45 (s, 12 H), 1.80 (s, 4 H), 5.03 (s, 4 H), 7.33 (s, 4 H)	25.73 (q), 34.26 (p), 68.28 (t), 83.83 (s), 128.39 (d), 153.22 (s)
VIc	1742, 1454, 1388, 1371, 1260, 1162	1.43 (s, 12 H), 1.78 (m, 4 H), 5.00 (s, 4 H), 7.28 (s, 4 H)	25.74 (q), 34.26 (m), 68.40 (t), 128.37 (d), 128.16 (d), 128.79 (d), 135.98 (s), 153.20 (s)
VId	1745, 1472, 1455, 1374, 1254, 1209, 1089	1.53 (s, 12 H), 1.90 (s, 4 H), 4.95 (s, 4 H)	25.63 (q), 34.36 (m), 54.52 (t), 80.90 (s), 84.51 (s), 152.55 (s)
VIe	1739, 1515, 1488, 1453, 1393, 1372, 1206, 1162, 1082, 859, 839	1.39 (s, 12 H), 1.50 (d, 6 H), 1.72 (m, 4 H), 5.53 (q, 2 H), 7.26 (s, 4 H)	22.35 (q), 34.01 (p), 75.34 (d), 83.64 (s), 126.14 (d), 141.26 (s), 152.68 (s)
VIf	1739, 1471, 1454, 1387, 1371, 1261, 1203, 1162, 1084, 867, 792	1.43 (s, 12 H), 1.80 (s, 4 H), 5.00 (s, 4 H), 7.30 (s, 4 H)	25.73 (q), 34.22 (m), 68.25 (t), 83.74 (s), 127.99 (m), 128.13 (m), 135.82 (s), 136.03 (s), 153.22 (s)
VIg	1740, 1476, 1443, 1372, 1258, 1262, 1207, 1167, 1085	1.47 (s, 12 H), 1.85 (s, 4 H), 4.72 (s, 1.2 H), 5.10 (s, 2.8 H), 7.40 (s, 2.8 H)	25.72 (q), 34.27 (t), 54.51 (t), 68.30 (t), 80.92 (s), (83.84) (s), 84.54 (s), 128.39 (d), 135.80 (s), 152.54 (s), 153.21 (s)

material has spectroscopic and elemental analyses consistent with the desired product. The product must not be left at room temperature for prolonged periods time, as decomposition by elimination occurs slowly; it is best stored at freezer temperature.

(2) Preparation of Polycarbonate VIb from III. A solution consisting of 3.0000 g (8.980 mmol) of the bis(carbonylimidazolide) III in 5 mL of dry THF under argon was treated with 1.2410 g (8.980 mmol) of *p*-benzenedimethanol along with 0.16 of 18-crown-6 and 6.4 g of finely powdered anhydrous potassium carbonate. The reaction mixture was then stirred vigorously while heated in an oil bath at 60 °C. During the first 3 h of stirring, there was a rapid increase in the viscosity of the mixture. TLC showed that most of III had disappeared and free imidazole was formed. The reaction mixture was stirred at 60 °C overnight to ensure high conversion. The workup was done by diluting the reaction mixture with methylene chloride and centrifuging the suspension. The decanted clear solution was then filtered and most of the solvent was removed by evaporation. Final recovery of the polymer was accomplished by precipitation in methanol. After reprecipitation, the polymer was washed several times with methanol and dried in vacuo overnight. In this way, 1.86 g (79.4% yield) of white polymer was recovered. The polymer has elemental (Table I) and spectroscopic (Table III) analyses consistent with the expected linear alternating polycarbonate of 2,5-dimethyl-2,5-hexanediol and *p*-benzenedimethanol. The polymer is soluble in methylene chloride, 1,2-dichloroethane, and chloroform, but insoluble in THF, 2-methoxyethyl acetate, bis(2-methoxyethyl) ether, and ethylene glycol dimethyl ether.

(3) Preparation of Polycarbonate VIc from III. This polymer was prepared as described above for VIb using *m*-benzenedimethanol and III (9 mmol of each) in refluxing dichloromethane to yield a methanol-soluble polymer which was isolated by washing an ethereal solution with water to remove imidazole, followed by chromatography to remove any low molecular weight contaminants. The final purified polymer isolated in ca. 64% yield is a clear tacky material that has spectroscopic and elemental analyses in accord with the proposed structure (see Tables I and III).

(4) Preparation of Oligomeric Carbonate VIa from III. The polymerization of III with 2,5-dimethyl-2,5-hexanediol was attempted as described above for VIb. The reaction was sluggish and much unreacted III and Va remained after 12 h. After 48 h of stirring in refluxing dichloromethane, III was entirely consumed while some product of thermal elimination (IV, Scheme II) could be detected in the reaction mixture. After workup as above for VIc, ca. 70% of tacky material was obtained. Spectrometric analysis of the product shows it to be a mixture of oligomeric carbonates with hydroxyl end groups.

(5) Preparation of Polycarbonate VId from III. This polymer was prepared as described for VIc. It was obtained in 70% yield as a clear soft material with spectral characteristics consistent with the proposed structure.

(6) Preparation of Polycarbonate VIf from III. A solution of 20.000 g (59.85 mmol) of III, 1.6539 g (11.97 mmol) of *m*-benzenedimethanol, and 6.6155 g (47.88 mmol) of *p*-benzenedimethanol in 20.0 mL of dichloromethane was treated under argon with 1.2 g of 18-crown-6 and 40 g of powdered anhydrous potassium carbonate. The mixture was heated in an oil bath at 65 °C with vigorous stirring for 1 h, after which the viscosity of the mixture had increased greatly and TLC showed only traces of the starting material remaining together with a considerable amount of imidazole. Stirring was continued overnight in a bath at 65 °C to ensure complete reaction. After workup as in the case of VIb, 16.78 g (83.9%) of reprecipitated VIf was obtained as a white powder with characterization data in agreement with the proposed structure (Tables I and III). The composition of the polymer is best confirmed by ^{13}C NMR using a comparison of the peaks at 136.03 and 135.83 ppm, which correspond to the meta and para isomers of benzenedimethanol, respectively. This analysis indicates incorporation of 21% *m*-benzenedimethanol, which corresponds to the initial feed (20% meta isomer) within experimental error. The composition of the polycarbonate was also confirmed by data obtained on VIf by GC–MS during the study of its thermal degradation.

Unlike polycarbonate VIb, obtained from *p*-benzenedimethanol, which is only soluble in halogenated solvents, polymer VIf, which contains 20% *m*-benzenedimethanol, is soluble in THF, diglyme, ethylene glycol dimethyl ether, and a variety of other organic solvents. The same procedure was used to prepare several other polycarbonates containing different proportions of *m*- and *p*-benzenedimethanol. The composition of VIf is nearly ideal, as the polymer retains a high melting point while acquiring improved solubility properties. The use of higher proportions of *m*-benzenedimethanol results in a drastic lowering of the melting point of the polymer.

(7) Preparation of 1,4-Bis(1-hydroxyethyl)benzene. A solution of 40 g (0.247 mol) of *p*-diacetylbenzene in 560 mL of methanol was treated slowly and with stirring with excess sodium borohydride while the reaction temperature was kept between 18 and 25 °C. After 1 h of stirring, TLC indicated that the reaction was complete. The methanol was evaporated and the residue dissolved in ether. The ethereal solution was washed with brine and dried over magnesium sulfate. Evaporation of the solvent yielded a crude product, which was recrystallized from ethyl acetate/petroleum ether to afford 31.1 g (77%) of white crystals with mp 86–88 °C and spectral characteristics consistent with those expected for the pure compound: ^{13}C NMR 25.24 (9, CH_3), 69.3 (d, CHO), 125.37 (d, CH aromatic), 145.09 (s, C aromatic); ^1H NMR 1.47 (d, 6 H, CH_3), 2.28 (s, 2 H, OH exchangeable), 4.80 (9, 2 H, CHO), 7.23 (s, 4 H, CH aromatic); IR 3327, 1368, 1303, 1211, 1072, 1007, 831, 790 cm^{-1}; MS *m/e* 166 (M^+), 151, 133, 121, 105, 91, 77.

(8) Preparation of Polycarbonate VIe from III. The reaction was carried out as described for VIb using 60 mmol of 1,4-bis(1-hydroxyethyl)benzene and 60 mmol of III in 20 mL of refluxing dichloromethane. Workup of the polycarbonate afforded 15.4 g (71% yield) of a white polymer with analytical and spectral characteristics in agreement with the proposed structure (Tables I and III). The polymer is soluble in a wide variety of solvents, including THF, diglyme, toluene, and halogenated hydrocarbons.

(9) Thermolysis of the Polycarbonates. The thermolysis reactions were monitored by both TGA and GC–MS techniques. All of the products of the thermolysis were volatile and no solid residue was observed. In the case of the GC–MS experiments, the thermolysis products were separated on appropriate capillary columns prior to mass spectral analysis. Direct MS analysis without prior separation afforded composite spectra with identical features.

Acknowledgment. Partial support of this research by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. In addition, we thank IBM Corp. for a research grant under the SUR program, Mr. Gui Bazan of the University of Ottawa for assistance in the synthesis of polymer VIg, Dr. Clement Kazakoff of the University of Ottawa Regional Mass Spectrometry Center for assistance in the GC–MS studies, and Mr. Richard Siemens of the IBM Research Division for the DSC and TGA analyses. We thank the referees for their helpful suggestions.

Registry No. III, 98716-64-4; (III)·(*m*-benzenedimethanol) (copolymer), 99214-22-9; (III)·(2,5-dimethyl-2,5-hexanediol) (copolymer), 99214-23-0; (III)·(*p*-benzenedimethanol) (copolymer), 99214-21-8; (III)·(1,4-butynediol) (copolymer), 99214-24-1; (III)·(*m*-benzenedimethanol)·(*p*-benzenedimethanol) (copolymer), 99214-25-2; (III)·(1,4-bis(1-hydroxyethyl)benzene) (copolymer), 99214-26-3; (III)·(*p*-benzenedimethanol)·(1,4-butynediol) (copolymer), 99214-27-4; VIa (SRU), 99214-35-4; VIb (SRU), 98716-42-8; VIc (SRU), 99214-34-3; VId (SRU), 99214-36-5; VIe (SRU), 99214-37-6; VIf (SRU), 99280-54-3; 2,5-dimethyl-2,5-hexanediol, 110-03-2; 1,1′-carbonyldiimidazole, 530-62-1; *p*-diacetylbenzene, 1009-61-6; 1,4-bis(1-hydroxyethyl)benzene, 6781-43-7.

References and Notes

(1) Taken in part from the Ph.D. thesis of F. M. Houlihan, University of Ottawa, 1984.
(2) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* **1983**, *24*, 995.
(3) Ito, H.; Willson, C. G.; Fréchet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510.
(4) Bodansky, M.; Klausner, Y. S.; Ondetti, M. A. "Peptide Synthesis", 2nd ed.; Wiley: New York, 1976.
(5) Houlihan, F. M.; Bouchard, F.; Fréchet, J. M. J.; Willson, C. G. *Can. J. Chem.* **1985**, *63*, 153.
(6) Carpino, L. A. *J. Am. Chem. Soc.* **1957**, *79*, 98. Gutte, B.; Merrifield, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 501.
(7) Bailey, W. J.; Griffith, J. R. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1964**, *5*, 279.
(8) Overberger, C. G.; Daly, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 3402. Daly, W. H.; Lee, C. S. "Reactions on Polymers"; Moore, J. A., Ed.; Reidel Press: Boston, 1973.
(9) Choppin, A. R.; Rogers, J. W. *J. Am. Chem. Soc.* **1948**, *70*, 2967.
(10) Woodward, R. B.; Heusler, K.; Gosteli, H.; Naegeli, P.; Oppolzer, W.; Ramage, R.; Ranganathan, S.; Vorbrugen, H. *J. Am. Chem. Soc.* **1966**, *88*, 852.
(11) Staab, H. A.; Mannschreck, A. *Chem. Ber.* **1962**, *95*, 1284. Staab, H. A. *Justus Liebigs Ann. Chem.* **1951**, *609*, 75.
(12) Corey, E. J.; Winters, R. A. E. *J. Am. Chem. Soc.* **1963**, *85*, 2677. Nagabhuschan, T. L. *Can. J. Chem.* **1970**, *48*, 383.
(13) Under a variety of reaction conditions such as phase-transfer catalysis or base catalysis with alkoxide generated from sodium and the diol, pinacol reacts with the carbonylimidazolide of benzyl alcohol to afford the cyclic carbonate, imidazole, and benzyl alcohol.

Mechanism of Phase-Transfer-Agent-Aided Free Radical Polymerization Using Potassium Peroxydisulfate Initiator and Tetrabutylammonium Bromide Phase-Transfer Agent

Narendra N. Ghosh and Broja M. Mandal*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India. *Received December 12, 1984*

ABSTRACT: The kinetics of the phase-transfer-agent-aided free radical polymerization of styrene has been investigated at 60 °C by using $K_2S_2O_8$ initiator, tetrabutylammonium bromide (Bu_4NBr) phase-transfer agent, and o-dichlorobenzene solvent. The rate of polymerization was found to be proportional to $[K_2S_2O_8]^{1/2}$·$[Bu_4NBr]^{1/2}$ and to (volume of the aqueous phase)$^{1/2}$ at constant volume of the organic phase. Analysis of the organic phase showed that the extent of phase transfer of the divalent $S_2O_8^{2-}$ is greater than that of the monovalent bromide ion, although the amount transferred is very small. The kinetic results fit in a polymerization mechanism that considers the phase-transferred $SO_4^{-}\cdot$ ion radical as the predominant initiating species instead of the phase-transferred $S_2O_8^{2-}$ acting as the principal initiator. The end-group analysis by dye extraction test indicated the presence of $SO_4^{-}Bu_4N^+$ end groups in the polymers.

Introduction

There has been considerable interest in recent years in phase-transfer-agent-aided free radical polymerization of vinyl monomers using water-soluble peroxydisulfates as initiators and crown ethers or quaternary ammonium salts (QX) as phase-transfer (PT) agents.[1-6] The mechanism for the rapid polymerization in the presence of PT agents that seems obvious involves the transfer of the peroxydisulfate anion from the aqueous phase to the monomer-containing organic phase by PT agents (eq 1), where the former initiates polymerization following its decomposition to sulfate anion radical (eq 2).[1-3] For the quaternary PT agent this mechanism may be symbolically written as follows:

$$Q^+_w + X^-_w \overset{K_x}{\rightleftharpoons} Q^+X^-_o \quad (1)$$

$$2Q^+_w + S_2O_8^{2-}{}_w \overset{K_p}{\rightleftharpoons} Q_2^+S_2O_8^{2-}{}_o \quad (2)$$

$$Q_2^+S_2O_8^{2-}{}_o \xrightarrow{k_d} 2Q^+SO_4^{-}\cdot{}_o \quad (3)$$

$$Q^+SO_4^{-}\cdot{}_o + \text{monomer (M)}_o \rightarrow Q^+ {}^-O_3SO\text{–}\dot{M}_o \text{ etc.} \quad (4)$$

where X^- is Cl^-, Br^-, HSO_4^-, etc. and the subscripts o and w refer to the organic phase and aqueous phase, respec-

0024-9297/86/2219-0019$01.50/0