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EFFECT OF ULTRASOUND ON SYNTHESIS OF A POLYCARBONATE [1]

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ABSTRACT

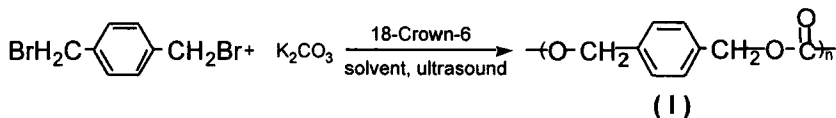
Effects of ultrasound (US) on the synthesis of poly(p-xylylene carbonate) [1] by crown ether mediated reactions of a,a'-dibromo- and dichloro-p-xylenes with potassium carbonate at ambient temperatures for 12, 18 and 24 h in diglyme, DMF, chlorobenzene, and NMP solvents were compared with syntheses in the absence of US at elevated temperatures. No polymer was formed with the dibromide in 24 h at ambient temperature in the absence of US. With US, yields and M_n increased to a maximum with time and then decreased because of polymer chain fragmentation. A maximum yield of 56% with $M_n = 2500$ was obtained with US in DMF in 18 h. No polymer was formed in 60 h in DMF at 80 or 120 °C in the absence of US. The maximum M_n of 4300 was for polymer formed in 18 h in diglyme; however, the yield was only 2%. Results in other solvents (Tables 1-3) were intermediate. US reactions with the dibromo

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compound were much faster than with the dichloro analog. Mechanisms for US-induced fragmentations are proposed.

INTRODUCTION

Effects of ultrasound on syntheses of a variety of compounds have been studied [2-5] but lesser attention has been devoted to the effect on syntheses of polymers [6-10]. Most of these studies have dealt with chain reaction polymerization of vinyl monomers [5, 10, 12, 13] and only a few recent scattered references to step-reaction polymerization have appeared; these were on the preparation of polysilanes [14-17]. In view of the abundant availability of carbon dioxide as a carbon source, we have been exploring its incorporation into a polycarbonate as an example of a useful material [18]. Polycarbonates are commercially useful as safety shields, bullet-proof windows, safety helmets etc. In order to avoid the use of toxic phosgene usually used in polycarbonate syntheses with dihydroxy alcohols or phenols, other starting materials such as carbon dioxide or its derivatives including metallic carbonates are desirable. The synthesis of poly(p-xylylene carbonate) [1]** was selected as a well-characterized [19-28] polycarbonate convenient to synthesize for our initial studies. Reactions with active dihalides such as dihalo-p-xylenes were based on our successful syntheses of other polyesters from reactions of halo acids mediated by tertiary amines [29-34] and dihalides with dicarboxylic acids [35]. Since all reactants were not soluble in any suitable solvents, a crown ether was necessary for this heterogeneous phase-transfer catalytic system. Ultrasound had been shown to be effective in promoting other heterogeneous reactions in the synthesis of polysilanes [14-16]. The use of ultrasound on the present system (eqn.) was to determine whether it might be effective in shortening the time of reaction and its effect on the yields and molecular weights of the products.



**Systematic name: Poly(oxycarbonyloxymethylene).

EXPERIMENTAL

Materials and Instrumentation.

All reagents and solvents were procured from commercial sources in the following purity grades and were used as received: dibromo-*p*-xylene (97%), dichloro-*p*-xylene (98%), 1-methyl-2-pyrrolidinone (99.5%), dimethylformamide (99.8%), diglyme (99.5%), and chlorobenzene (99+%). Ultrasound-induced reactions were carried out in a Fisher FS9,43 kHz, 55 W ultrasonic cleaning bath. ^1H and ^{13}C -NMR spectra were run on a Bruker AMX-360 FT spectrometer. Compounds were dissolved in a CDCl_3 /trifluoroacetic acid-*d* solvent system [34, 35] with TMS as internal standard. Infrared spectra, with samples taken as pressed KBr pellets, were obtained using a Mattson CYGNUS 100 FTIR spectrophotometer. Melting points were taken in glass capillary tubes using a Unimelt Thomas Hoover melting point instrument.

Reactions.

To a round-bottom flask flushed with argon was added dibromo-*p*-xylene (1.00 g, 3.79 mmole), potassium carbonate (0.56 g, 3.98 mmole), 18-crown-6 (0.25 g, 0.95 mmole), and 3 mL of solvent. The capped flask was immersed in an ultrasonic cleaning bath filled with water at room temperature. On termination of the reaction, work-up was performed by washing in succession with water, ether, and methanol. The resulting yellow powder was then dried *in vacuo* at room temperature for about 12 h. For reactions by conventional heating, the same measured quantities were placed in a round-bottomed flask containing a magnetic spin bar and immersed in an oil bath at 80 °C or 120 °C. Work-up was performed in the same manner as the ultrasound-induced reactions. The reaction products were insoluble at room temperature in common organic solvents and soluble only in hot dimethylsulfoxide. IR, ^1H and ^{13}C -NMR spectra of the products of both the ultrasound and heat-induced reactions were the same (differing only in integral values of the peaks) as indicated: ^1H NMR (CDCl_3 /TFAA-*d*; *d*) : 7.37 (s, Ar-H); 5.22 (CH₂O), 4.68 (s, CH₂Br), 4.48 [lit. (22) 7.38, 5.18, 4.52 respectively Ar-H, CH₂O, CH₂Br]; ^{13}C NMR (CDCl_3 /TFAA-*d*; *d*) : 156.44 (C=O), 135.12 (ipso-Ar), 129.21 (Ar-CH), 70.65 (CH₂Br); IR (KBr, cm^{-1}) : 3033 (arom str), 2968 (C-H str), 1744 (OC(=O)O str), 1258, 1233 (C-O str), 756 (C-Br str); [lit. (22) 1745-1750, 1235-1280, 760 respectively C=O, C-O, C-Br str.; (25) 1740, 1260; (28) 1745, 1230-1280].

M_n values were obtained by ^1H NMR end group analysis, dividing the integral of the polymer peak at 5.22 by the integral of the end-group peak at 4.68, then multiplying by the molecular mass, 164, of a repeating unit. Melting points for the ultrasound-induced reaction products all fell between 153-160 °C while those for the heat-induced reaction were between 200-206 °C.

RESULTS

α, α' -Dibromo-*p*-xylene.

Effect of ultrasound.

The products after workup were light-yellow powders. T_m values for all samples ranged between 153 and 160 °C {lit mp °C, 177-185 (19); 141 min to >300 depending on conditions [24]}. In DMF and chlorobenzene, maximum yields of 56 and 25% respectively were obtained at the 18 hour period of reaction with a decrease in yields at the 24 hour reaction period (Table 1). In diglyme a maximum yield of 14% was obtained in 24 hours whereas for NMP no product was obtained in any of the time periods. With respect to the molecular weights of the products, the highest values in all solvents were obtained for the 18-hour reaction products with a decrease for the 24-hour products. For diglyme, chlorobenzene, and DMF the values for M_n were 4300, 3600, and 2500 respectively. This is a reverse order with respect to the yields obtained in these solvents. It is evident that chain degradation takes place in all solvents studied after 18 hours reaction time to yield lower molecular weight fragments.

A more exact determination of the optimum time for yield and molecular weight could be obtained by conducting experiments in the time interval between 12 and 24 hours. Further improvements in selectivity between bond-making and -breaking might be made if instruments were available for varying the ultrasound frequency.

Effect of temperature.

No polymer was formed at ambient temperature in 24 hours with the dibromide in DMF in contrast with the US synthesis in this solvent where the maximum yield was obtained. In chlorobenzene solvent an increase in yield from 24 to 45% was obtained at temperatures of 80 and 120 °C respectively for the same time period of reaction of 60 h (Table 2). However, the values for M_n decreased from 2600 to

TABLE 1

Results of ultrasound-induced phase-transfer polymerization of α,α' -dibromo-p-xylene with potassium carbonate.

Solvent	t (h)	Yield (%)	M_n
DMF	12	12	82
"	18	56	250
"	24	40	160
Chlorobenzene	12	7	160
"	18	25	360
"	24	11	340
Diglyme	12	3	410
"	18	2	430
"	24	14	200
NMP ^a	12,18,24	----	----

^aN-Methylpyrrolidone

TABLE 2

Results of heat-promoted phase-transfer polymerization of α,α' -dibromo-p-xylene^a with potassium carbonate.

Solvent	Temp ^b (°C)	Yield (%)	M_n
DMF	80	trace	----
"	120	trace	----
Chlorobenzene	80	24	2600
"	120	45	1800
Diglyme	80	15	2500
"	120	5	3600

^aReactions run for 60 h., ^bTemperature of oil bath.

1800 respectively for the two temperatures. For diglyme, the yields for the 80 and 120 °C reactions were 15 and 5% respectively with corresponding M_n values of 2500 and 3600. In many cases it can be noted that the lower the yield, the higher the M_n value. However, no explanation seems evident for this observation and this qualitative relationship is not consistent for all cases. T_m values for the products from the thermal reactions were 200-206 °C, higher than those from US reactions or literature reports [19, 24]. Since M_n values and NMR spectra are not much different between the samples, a reasonable explanation cannot be offered at this stage of the study.

α,α' -Dichloro-p-xylene.

Effect of ultrasound.

The reactions carried out in three solvents for periods of 12, 18, and 24 h showed a markedly lower reactivity of the chloro compound as compared with the bromo. No products were obtained in chlorobenzene or NMP (Table 3). In DMF low yields of 4 and 7% were obtained in 12 and 18 h respectively with corresponding M_n values of 4300 and 2500 which are in accord with the approximate inverse correlation referred to above between yield and M_n .

DISCUSSION

With ultrasound, the highest yield of 56% was obtained in DMF in 18 hours. This yield could probably be improved by a study of the reaction times either before or after 18 hours. The molecular weight of 2500 at 18 hours, however is not as high as the molecular weights of 3600 in chlorobenzene at 18 hours or the value of 4300 in diglyme. However, the yields of product are much lower in the latter two solvents. It should be emphasized that the ultrasound reactions were carried out at ambient conditions and the time for obtaining maximum results was considerably less than for reactions at elevated temperatures of 80 or 120 °C for about 60 hours. One surprising result was that only a trace of product was isolated in DMF at either temperature where ultrasound was not employed whereas this was the best solvent with ultrasound at ambient temperatures.

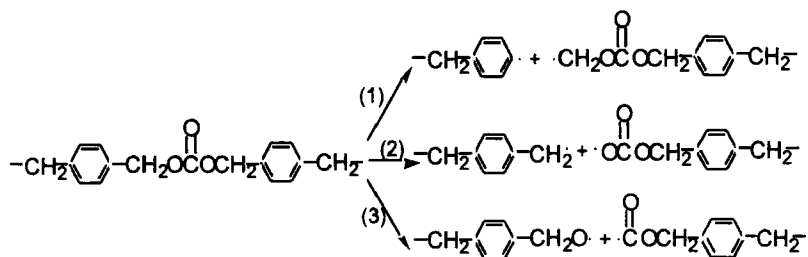
Mechanisms for the usual phase-transfer aspect of the syntheses have previously been given [24, 26] but the role of the solvent was not taken into account. With

TABLE 3

Results of ultrasound-promoted phase-transfer polymerization of a,a'-dichloro-p-xylene with potassium carbonate.

Solvent	t(h)	Yield (%)	M _n
DMF	12	4	4200
"	18	7	2500
"	24	---	---
Chlorobenzene	12,18,24	---	---
NMP	12,18,24	---	---

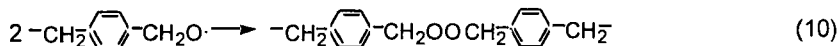
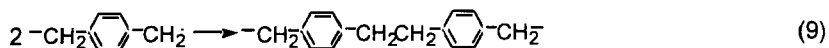
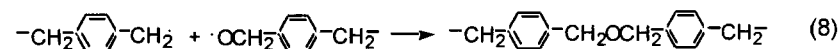
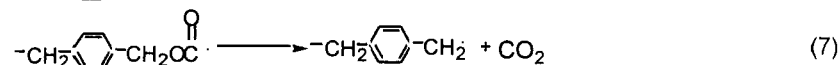
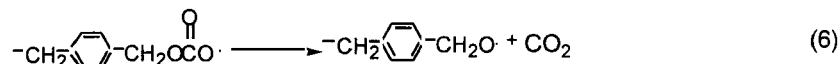
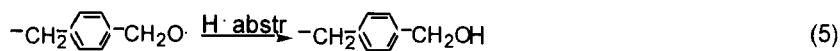
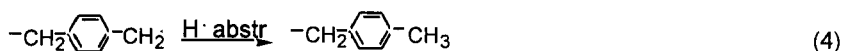
ultrasound, cavitation is thought to occur and generate very high local pressures in excess of 1000 atm. [38] and temperatures as high as 7000 °K [39]. Degradation of the polymer evidently begins to occur at some stage after it is formed as evidenced by a decrease observed in M_n with time after 18 h. Ultrasonic studies of other types of polymer degradation have been carried out previously. Homolytic cleavage of the polymer molecules is thought to occur at about the center of the molecules to form radicals which then react further in predictable fashion. For the present polymer, three modes of fragmentation (eqs. 1-3) can be considered:



The macroradicals formed would be expected to undergo further reactions including hydrogen abstraction (eqs. 4,5) to form stable p-tolyl- and benzyl-type

end groups. Decarboxylation (eqs. 6,7) would form the same macroradicals as in eqs. 4 and 5. Macroradical combination as a termination process would be expected to form ethers (eq. 8), $-\text{CH}_2\text{CH}_2-$ linkages (eq. 9), or peroxides (eq. 10). In the later stages of the sonication reactions, weak signals in the ^1H NMR spectra in addition to the ones expected for poly(p-xylylene carbonate) begin to appear.

McNeill and Rincon [36] and Montaudo et al. [37] have recently studied the thermal degradation of poly(p-xylylene carbonate), the former workers by thermogravimetry, DSC, and thermal volatilization analysis and the latter group by electron impact/chemical ionization and direct pyrolysis mass spectrometry. The two groups differ in the interpretation of the mechanisms of decomposition. McNeill and Rincon [36] propose formation of macroradicals by chain homolysis whereas Montaudo et al. propose ionic processes.



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