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Preparation of Polymers under Phase-Transfer Catalytic Conditions

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Abstract:

The application of phase-transfer catalytic (PTC) conditions leading to substantial improvements in numerous polymerization reactions is described. Generally, better yields as well as faster and cleaner reactions are achieved compared to reactions under conventional conditions. Owing to their ionic mechanisms, polycondensation reactions are the most often applied among polymerization methods under PTC conditions; thus, a number of examples on gram scale are presented in this review.

Introduction

Phase transfer catalysis (PTC) is one of the most useful techniques available when anionic activation is concerned. It has been used in over 600 industrial processes in areas such as intermediates, dyestuffs, agrochemicals, perfumes, flavours, pharmaceuticals, and polymers and value exceeds $12 billion (U.S.) per year.[1-4] However, the effluent-treatment problem associated with a soluble PTC has hampered exploitation of PTC on scale. Thus, the applications of PTC are often confined to the synthesis of low-volume and high-cost specialty, agricultural and pharmaceutical chemicals.[5] The reactions in which PTC catalysis has been successful include such important chemical transformations as C-, N-, O-, and S-alkylations, etherification, esterification, transesterification, condensation, carbene reactions, nucleophilic displacements, oxidation, epoxidation, and polymerization. Therefore, it should be stressed that in this contribution it is not our intention to review a great number of papers reporting the use of PTC catalysis for polymer synthesis in industrially important reactions, but rather to give representative examples to demonstrate the scope and usefulness of these reactions provided that they were performed in higher scale than 1.0 g of substrates.

Polymerization under Phase-Transfer-Catalytic Conditions. Among polymerization methods under PTC conditions, polycondensation reactions are the most often applied owing to their ionic mechanisms. However, the polycondensation process under PTC is a complex process, accompanied by an increase in the viscosity of the organic phase which results from increasing polymer concentration and from the change of its properties (i.e., average molecular weight of polymer, M_w, and polydispersity index, PI). The rate of the reverse reaction creating the ionic pair, the mass transfer rate of catalyst from the organic to aqueous phase, the mass transfer rates of monomers to the reaction zone, and the rate of polycondensation reaction influence the overall rate of the process.[6] Which of these stages is the rate-limiting step for the polycondensation process has not yet been determined. According to Brzozowski et al.[7] and Tsai et al.,[8-12] the mass transfer rate of monomers into the reaction zone is the rate-limiting step of the whole process. Morgan and Kwolek[13] demonstrated that polycondensation reactions were fast reactions whose rate constants k were in the range of $102-106$ L/mol·s. However, Wang et al.[14] suggested that the chemical reaction in the organic phase is the rate-limiting step. In turn, Berezkin and Khokhlov,[15] on the basis of theoretical considerations, linked the molar ratio of used monomers and the degree of polymerization (P_n) with the regions in which the rate of the overall process is controlled by an appropriate stage, i.e., the mass transfer rate in the continuous phase, the mass transfer rate in the dispersed phase, or polycondensation reaction in the dispersed phase. It was shown that a high P_n is possible only for fast polycondensation reactions with a suitable molar ratio of monomers. In the case of slow reactions, the available degrees of polymerization are in the range of $P_n = 2-3$, independent of the molar ratio of monomers. Additionally, the influence of the monomer's concentration ratio, stirring rate, kind and quantity of the applied catalyst, and also temperature on the rate of a polycondensation process in a stirred tank reactor has been investigated by a number of authors.[7-14] In the polycondensation process, it was possible to obtain a comparatively high molecular weight of polymers: $M_w = 200-500 \times 10^3$ g/mol[7,9] and a low polydispersion index: PI $= 2-3$. It should be stressed that the

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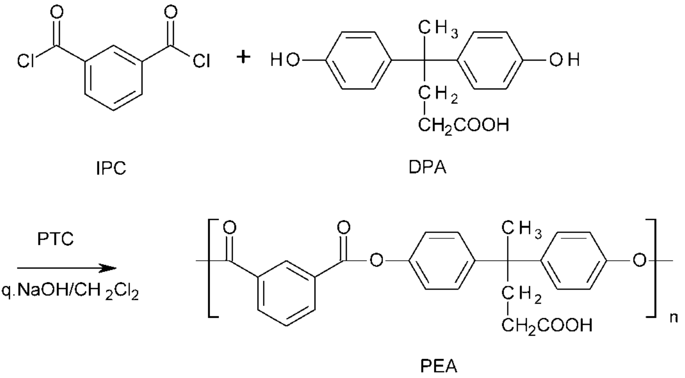

Figure 1. **Synthesis of aromatic polyesters with pendant groups.**

polycondensation process is also possible without the addition of a catalyst, but then the resulting molecular weights of polymers were considerably lower.[7,8]

Polyesters. A number of polyesters have been synthesized under PTC conditions and considerable attention has been paid to reactive aromatic polyesters. The aromatic polyesters having pendant functional groups are useful for applications such as polymer catalysts, amphoteric polyelectrolytes, chelating agents for metal ions, drug delivery systems and biodegradable polymers. For instance, the synthesis of aromatic polyesters by the polycondensation of isophthaloyl chloride (IPC) and diphenolic acid (DPA) under PTC conditions was studied, where quaternary ammonium halides and crown ethers were used as catalysts.[16] Several different copolyesters were also synthesized by adding other diols such as bisphenol A, 3-chloro-1,2-propanediol, *N*-ethyldiethanolamine to the above reaction mixture (Figure 1).

Polycondensation was carried out in a PTC system, in which 0.01 mol of isophthaloyl chloride (IPC) in 40 mL of dichloroethane was added to 0.01 mol of diphenolic acid (DPA) in 90 mL of 1 N aqueous NaOH solution in the presence of 0.1 g of PTC catalyst (Table 1). Then the mixture was stirred at 300 rpm and the reaction was continued for 1 h at 25 °C. The polyester (PEA) precipitated was filtered, washed by deionized water and then acetone, and dried in a vacuum.

The order of catalytic activity was determined as tetraoctylammonium chloride (TOAC) > tetrahexylammonium chloride (THAC) > tetrabutylammonium chloride (TBAC). Then, quaternary ammonium salts with different halide anion (Cl, Br, and I) were used to study the effect of the counteranion on the yield and molecular weight of the polyesters (PEA). The experimental results show that the molecular weight of the PEA increased in the order Cl <Br <I. In turn, the catalytic activity of the crown ether catalysts was lower than that of quaternary ammonium halide catalysts. As the carbon numbers of simple crown ethers increased from 15-crown-5 to 18-crown-6, the yield and M_w of the polyester increased (Table 1).

When different types of solvents were used for the synthesis of PEA, CH_2Cl_2, and CH_3Cl showed higher yield and molecular weight than the solvents like toluene and cyclohexane. Cyclohexane showed the lowest yield and less than 3000 g/mol of M_w value since the monomer IPC was poorly soluble in cyclohexane.

Table 1. **Yield and molecular weight of polyester (PEA) obtained from isophthaloyl chloride (IPC) under various reaction conditions and PTC catalysts[a]**

PTC[b]	reaction media	yield (%)	M_w[c] (g/mol)
TOAC	H_2O/CH_2Cl_2	77.0	26 100
THAC	H_2O/CH_2Cl_2	76.9	22 300
TBAC	H_2O/CH_2Cl_2	75.6	20 800
TBAB	H_2O/CH_2Cl_2	75.3	25 800
TBAI	H_2O/CH_2Cl_2	79.2	30 600
15-C-5	H_2O/CH_2Cl_2	15.6	8 500
18-C-6	H_2O/CH_2Cl_2	32.5	12 500
DCH-18-C-6	H_2O/CH_2Cl_2	24.3	8 500
DB-18-C-6	H_2O/CH_2Cl_2	19.3	6 700
TBAC	H_2O/chloroform	78.9	20 000
TBAC	H_2O/toluene	40.6	18 600
TBAC	H_2O/cyclohexane	12.3	9 800

[a] Reaction was carried out with 0.01 mol of IPC in 40 mL of CH_2Cl_2 and 0.01 mol of DPA in 90 mL of aqueous 1 N NaOH solution using 0.1 g of PTC at 25 °C for 1 h. [b] TOAC = tetraoctylammonium chloride, THAC = tetrahexylammonium chloride, TBAC = tetrabutylammonium chloride, TBAB = tetrabutylammonium bromide, TBAI = tetrabutylammonium iodide, 15-C-5 = 15-crown-5, 18-C-6 = 18-crown-6, DCH-18-C-6 = dicyclohexano-18-crown-6, DB-18-C-6 = dibenzo-18-crown-6. [c] Weight average molecular weight measured by a GPC.

The polycondensation of DPA and IPC under PTC conditions in various organic solvents was recently investigated in the presence of tetrabutylammonium chloride (TBAC) as catalyst.[17] The interaction between the polymer and the solvents was quantitatively analyzed, and a reaction mechanism was proposed. Then, the reaction conditions were optimized, and poly(DPA−IPC) with high intrinsic viscosity was prepared in high yield (Figure 2).

In a typical reaction sodium hydroxide (0.03 mol), DPA (0.01 mol), and TBAC (0.117 g) were added into 90 mL water. Then 50 mL of CH_2Cl_2 solution containing 0.01 mol of IPC was quickly added to the resulting aqueous solution under stirring at 400 rpm. The reaction started immediately, forming a mass of capsule particles. After reaction at 25 °C for 1 h, a certain amount of sulfuric acid was added, to control the pH of the solution to about 3, and an acidified polyester product, poly(DPA−IPC), was obtained. The yield and intrinsic viscosity ($[\eta]$) of poly(DPA−IPC) are summarized in (Table 2).

Among the solvents examined, a maximum $[\eta]$ of 1.77 dL/g was reached for 1,1,2,2-tetrachloroethane, and a minimum $[\eta]$ of 0.68 dL/g was obtained for cyclohexane. For CH_2Cl_2, a maximum yield (95%) and a high $[\eta]$ (1.71 dL/g) were obtained.

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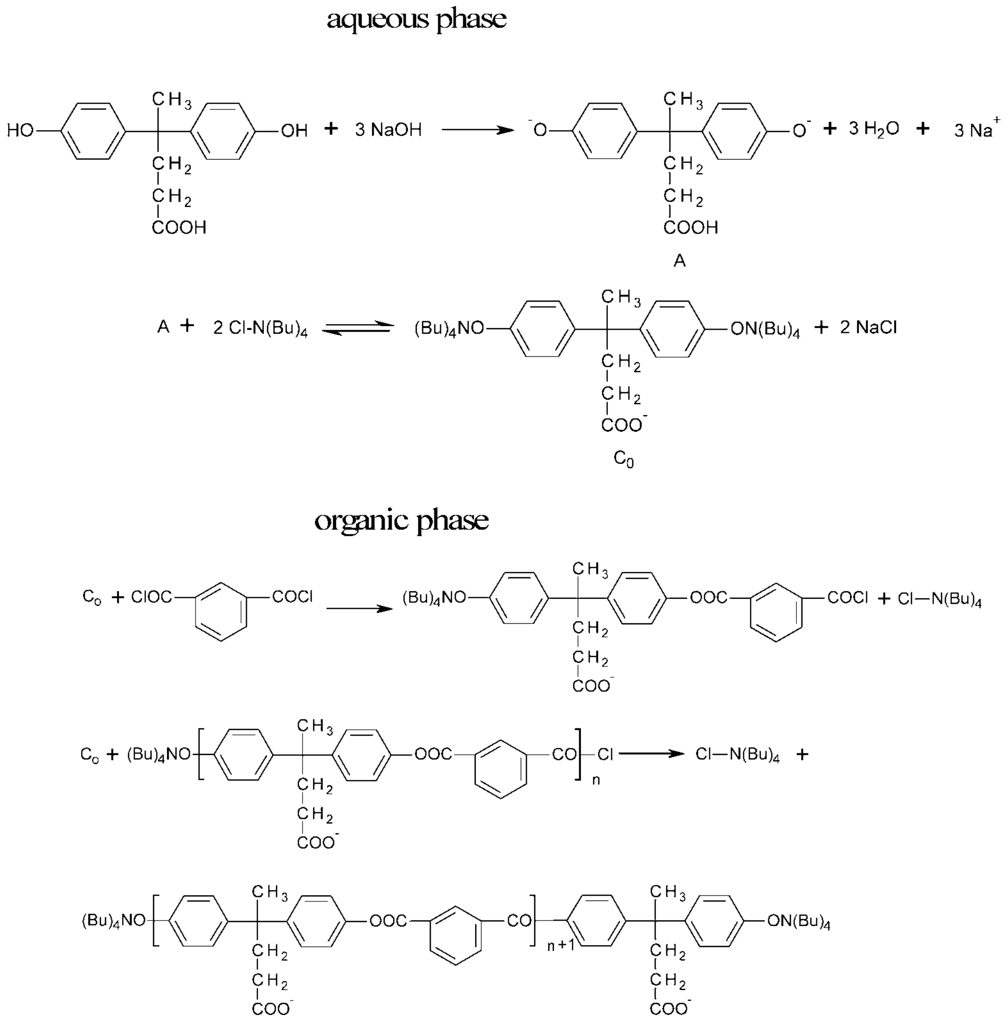

Figure 2. **Synthesis of aromatic polyesters; the basic reactions occurring in aqueous and organic phases.**

Table 2. **Interfacial polycondensation of DPA (diphenolic acid) and IPC (isophthaloyl chloride) in various solvents/aqueous media**[a]

	polymer		
solvent in organic phase	yield (%)	[η] (dL/g)[b]	*a* (mL/g)[c]
1,1,2,2-tetrachloroethane	87.4	1.77	4.25
chloroform	75.6	1.71	3.91
dichloromethane	95.0	1.71	3.71
1,2-dichloroethane	82.1	1.46	2.27
toluene	69.8	1.44	1.72
tetrachloromethane	52.7	0.95	1.59
cyclohexane	35.9	0.68	0.78

[a] Polycondensation conditions: 4% TBAC as catalyst, 25 °C, 1 h. [b] Intrinsic viscosity. [c] Swelling ratio of fresh poly(DPA−IPC) separated before acidification (namely, poly (DPA−IPC) with a pendent carboxylate salt group rather than a carboxyl group) in various solvents. The fresh poly(DPA−IPC) sample was prepared using dichloromethane as the solvent.

The yield for 1,1,2,2-tetrachloroethane was acceptable, but it is very low for cyclohexane. Clearly, CH_2Cl_2 was a preferable solvent for polymerization at small scale: 5 g of substrates; however, these conditions might be easily transferable to higher scale.

Aromatic polyesters containing biphenyl side groups were also synthesized in the reaction of of 1-(4-biphenylyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE) with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), and a mixture of TPC/IPC (50:50 mol ratio) (Figure 3).[18]

In a typical polymerization reaction, BBHPE (1.83 g, 5 mmol) was dissolved in 10 mL of 10 mmol NaOH. The mixture was stirred in a 100-mL flask for 1 h at 10 °C in. Next, benzyltriethylammonium chloride (TEBA) (30 mg) was added to the reaction mixture, and the stirring was continued. After 30 min, a solution of IPC (1.015 g, 5 mmol) in 20 mL of CH_2Cl_2 was added, and the mixture was stirred vigorously (2000 rpm) for 1 h. The reaction mixture was poured into hot water to precipitate the polymer, which was dissolved in CH_3Cl and reprecipitated into methanol. The yield of polyester was almost quantitative (Table 3).

The inherent viscosities of polyesters were in the range 0.44−1.26 dL/g indicating the formation of medium- to high-molecular-weight polymers (Table 3). This is also reflected in molecular weights of the polyesters measured by GPC. Finally, it was observed that transparent and flexible films could be cast from CH_3Cl solutions of these polyesters. Therefore, the polyesters containing biphenyl side groups may be considered as promising processable aromatic high-performance polymers.

The incorporation of sulfur into polymers results in the incorporation of improved mechanical properties and resistance

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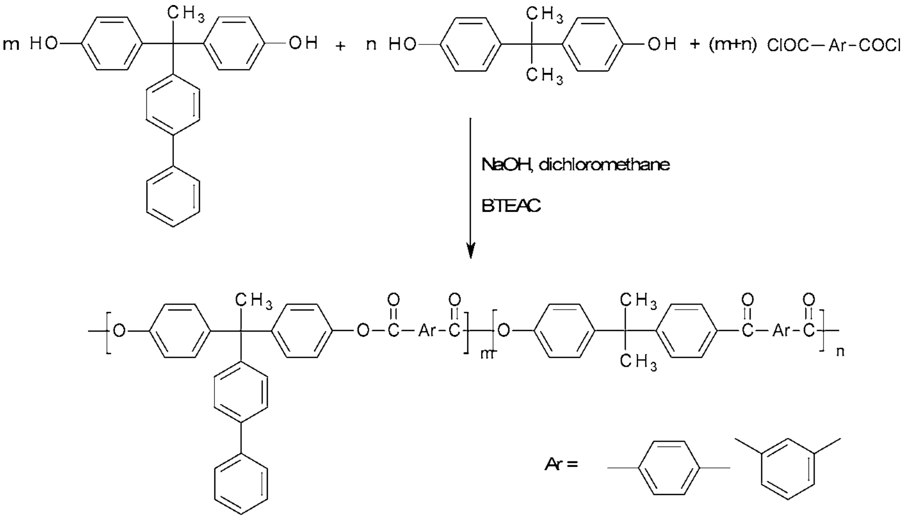

Figure 3. **Synthesis of aromatic polyesters containing biphenyl side groups.**

Table 3. **Synthesis and characterization of aromatic polyesters generated from the reaction of 1-(4-biphenylyl)-1,1-bis(4-hydroxyphenyl) ethane (BBHPE) with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC)**

composition of bisphenols (mol %)					
BBHPE	BPA	diacid chloride	η_{inh} (dL/g)[a]	M_n (g/mol)[b]	M_w (g/mol)[b]
100	0	TPC	0.56	25 800	57 000
75	25	TPC	0.49	19 150	38 850
50	50	TPC	0.7	37 750	64 750
25	75	TPC	1.26	66 600	160 200
100	0	IPC	0.45	13 650	29 950
75	25	IPC	0.47	21 100	44 550
50	50	IPC	0.48	31 700	60 150
25	75	IPC	0.7	52 500	98 350
100	0	IPC/TPC, 50:50	0.44	20 700	37 650

[a] Inherent viscosity measured in chloroform at a concentration of 0.5 g/dL at (30 ± 0.1)°C. [b] Molecular weights measured by size exclusion chromatography (SEC) in chloroform; polystyrene was used as a reference standard.

to heat and chemicals. The synthesis of sulfur-containing polyesters derived from bis(4,4-hydroxyphenyl)sulfide (TDP) and various acid dichlorides (AC) is possible under PTC conditions.[19] Polyesters derived from TDP and AC (with methylene numbers of 2−10) were synthesized by the polycondensation in a 1,1,2,2-tetrachloroethane/water solution in the presence of tetra-*n*-butylammonium bromide (TBAB) as a phase transfer catalyst (Figure 4).

In a typical reaction, TDP (~7.0 g, 50 mmol) was dissolved in 500 mL of aqueous NaOH solution (0.4 mol/L) in a 2-L flask. Then TBAB (2.5 mmol) was added to the solution, and a TCE (600 g) solution of acid dichloride (52.5 mmol) was slowly added through the funnel at 10 °C with vigorous stirring (8000 rpm). The mixture was stirred at room temperature for 30 min and separated into an aqueous and a cloudy organic layer. A white powder was precipitated out by pouring the organic layer into a large amount of methanol. For further purification, the polymers were dissolved in PhOH/TCE (1:1, w/w) and reprecipitated by pouring the solution into methanol. The polyesters yields were almost quantitative with a high molecular weight (M_w 27100−46400 g/mol) (Table 4).

The sulfur-containing polyesters exhibit very high gas-barrier properties against oxygen permeation. In particular, the polyesters with 3, 4, 6, and 8 methylene units (runs 2, 3, 5, and 7) had lower oxygen permeabilities than that of poly(ethylene-terephthalate) (PET), which is commonly used for such applications.

An interesting benzyltriethylammonium chloride (TEBA)-catalyzed procedure for the synthesis of UV-sensitive/curable polyarylates containing chalcone units was described by Brzozowski et al.[20] The monomers like 4,4′-dihydroxychalcone (BDHC) and 3-ethoxy-4,4′-dihydroxychalcone (BDHEC) reacted with a mixture of terephthaloyl chloride and isophthaloyl chloride to form polyarylates (Figure 5).

For this purpose, the mixture of bisphenols (i.e., BDHC and BDHEC) was combined with NaOH aq (0.2 mol of bisphenols mixture with 0.2 mol NaOH in 150 mL of water) in a 1 L reactor equipped with a thermometer and mechanical stirrer. Added into this solution was 0.02 mol TEBA in 50 mL of water. Then 0.2 mol of terephthaloyl chloride (2 parts) and isophthaloyl chloride (1 part) mixture in 300 mL of CH_2Cl_2 was poured slowly (30 min) to the solution at 20 °C. Next, 250 mL of CH_2Cl_2 was added (30 min), and an excess of NaOH was neutralized by addition of HCl (aq). After neutralization, the organic layer was separated and precipitated into 1 L of acetone. Finally, the polyarylates were separated in the form of white-yellow flocks and dried under vacuum (Table 5).

All the reaction products were studied as materials for photoresists. The dependence of UV absorption and tenacity were investigated as a function of irradiation time. After mechanical tests, the remaining content of R−CH═CH−R′ and R−CH═CH−(CO)−R′ groups were checked and the change due to irradiation was recorded. The plot of the dependence of the % of conversion (% of UV cross-linkable), % of isomeri-

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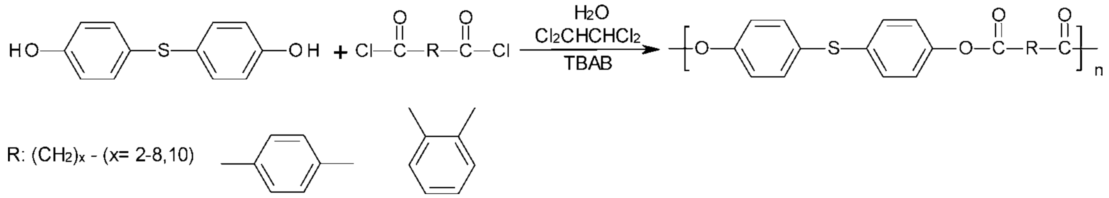

Figure 4. **Synthesis of polyesters containing sulfur bridges.**

Table 4. **Characterization of copolymers derived from TDP and several acid dichlorides**

acid dichloride	methylene number	yield (%)	η_{spn}[a] (dL/g)	M_n[c] ($\times 10^3$) (g/mol)	M_w[c] ($\times 10^3$) (g/mol)	P_d
succinyl	2	96	0.52	–[e]	–[c]	–[e]
glutaryl	3	94	0.38	10.0[d]	27.1[d]	2.71[d]
adipoyl	4	94	1.12	–[c]	–[e]	–[e]
pimeloyl	5	92	0.71	26.4[d]	46.4[d]	1.75[d]
suberoyl	6	91	0.64	–[e]	–[c]	–[e]
azelaoyl	7	93	0.68	21.7[d]	39.8[d]	1.84[d]
sebacoyl	8	96	0.56	–[e]	–[e]	–[c]
dodecandioyl	10	95	0.49	–[e]	–[e]	–[e]
isophthaloyl	–	95	0.79	–[e]	–[e]	–[c]
terephthaloyl	–	98	–[b]	–[e]	–[e]	–[c]

[a] 35 °C, PhOH/TCE = 1/3 (w/w), 1 g/dL. [b] Insoluble in PhOH/TCE. [c] Determined by SEC. [d] Soluble part in THF. [e] Insoluble in THF.

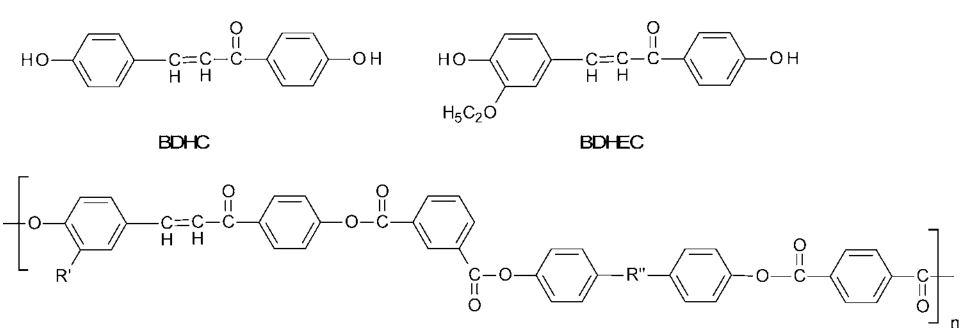

Figure 5. **Structures of monomers and UV-sensitive polyarylates containing chalcones units.**

Table 5. **Molar proportion of BDHC, BDHEC, and un-cross-linkable comonomers**[a]

DIAN	CBP II	BDHEC	BDHC	yield (%)
1	–	2	–	50.3
1	–	1	–	66.7
2	–	1	–	80.4
3	–	1	–	96.0
–	2	1	–	98.0
–	1	1	–	78.8
–	1	2	–	70.3
–	1	3	–	68.0
2	–	–	1	59.8
1	–	–	1	unknown
1	–	–	2	unknown
–	2	–	1	63.2
–	1	–	1	unknown
–	1	–	2	unknown

[a] BDHC = 4,4′-dihydroxychalcone; BDHEC = 3-ethoxy-4,4′-dihydroxychalcone.

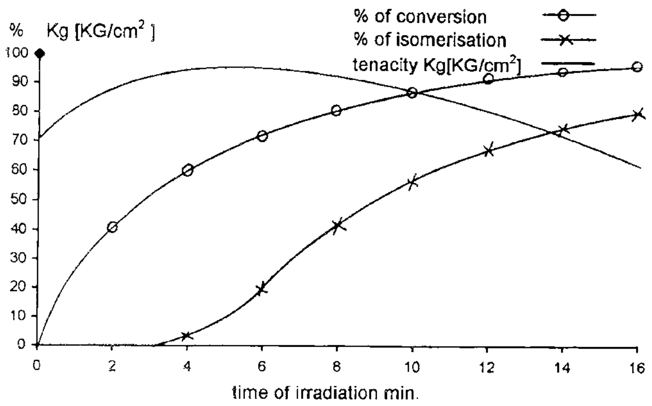

Figure 6. **Dependence % of conversion (% of UV cross-linkable), % of isomerisation and tenacity as a function of UV irradiation time for polymer PA53.**

sation, and tenacity as a function of UV irradiation time are shown in Figure 6.

Polycarbonates and Polythiocarbonates. Polycarbonates (PC) are some of the most widely used thermoplastics because of their high transparency, outstanding impact strength, ductility, superior dimensional stability, inherent fire resistance, and thermal stability. Polycarbonates are commonly formed by the phosgenation of (1) bisphenols, usually bisphenol A; (2) ester exchange between diaryl carbonates and bisphenols, usually between diphenyl carbonate and bisphenol A; or (3) interfacial polycondensation of phosgene and carbonates. Polycarbonates and polythiocarbonates from phosgene and thiophosgene, respectively, were synthesized from bisphenols with chlorinated aromatic side groups under PTC conditions using several quaternary ammonium and phosphonium salts and CH_2Cl_2 as a solvent.[21,22] In a typical polycondensation reaction, 5 mmol of the bisphenol and 0.25 mmol of the catalyst (i.e., TBAB, HDTMAB, BTEAC, HDTBPB, Aliquat 336) dissolved in 30 mL of 1 M NaOH were mixed with 20 mL of CH_2Cl_2. Then,

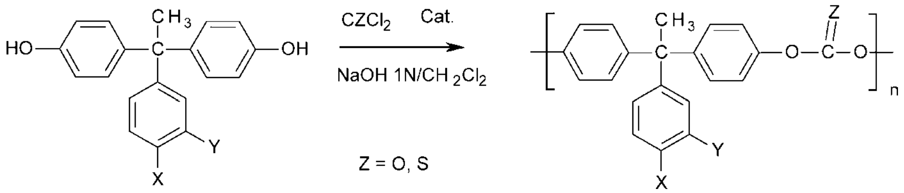

Figure 7. **Polycarbonates and polythiocarbonates were obtained according to the following reaction.**

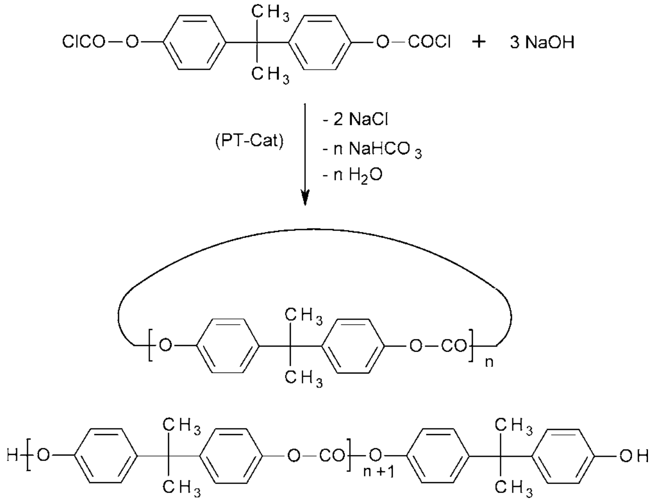

Figure 8. **Synthesis of polycarbonates and cycle polycarbonates.**

5 mmol of phosgene or thiophosgene dissolved in 10 mL of CH_2Cl_2 was added at once. The mixture was stirred at 20 °C for 30 or 60 min. The organic layer was separated and poured into methanol, and the precipitated polymer was filtered and dried under vacuum (Figure 7). Polycarbonates and polythiocarbonates were obtained with yields and inherent viscosities of the range of 66−94% and 0.08−0.34 dL/g, correspondingly.

In a more recent paper, polycarbonates were prepared by the polycondensation of bisphenol A−bischloroformate (BABC) performed under PTC conditions with four different catalysts: *N*-butylpyridinium bromide, triethylbenzylammonium chloride (TEBA), tetrabutylammonium hydrogen sulfate (TBAHS), and tetraphenylphosphonium bromide (Figure 8).[23]

These polycondensations were conducted at 5 or 35 °C as an initial reaction temperature. In a typical procedure, a solution of BABC (20 mmol) in dry CH_2Cl_2 (200 mL) and a solution of NaOH (84 mmol) in water (200 mL) was cooled to 4−5 °C. TEBA (4 mmol) was then added to the aqueous solution, and both solutions were mixed with a high-speed stirrer. Under external cooling with an ice/NaCl mixture, the internal temperature reached 15 °C after 10 min. Then stirring was continued for 50 min without cooling. The organic phase was diluted with CH_2Cl_2 (1 L) and precipitated into methanol. The resulting polycarbonates were characterized by viscosity and size exclusion chromatography (SEC) measurements and by matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry (Table 6).

Table 6. **Hydrolytic polycondensations of BABC catalyzed with various PTC catalysts**

catalyst	temp. (°C)	yield (%)	$\eta_{inh}{}^{a}$ (dL/g)	$M_{ei}{}^{b}$ (g/mol)
butylpyridinium bromide	5	56	0.26	<1 000
butylpyridinium bromide	35	56	0.11	<1 000
TEBA-Cl	5	65	5.23	>15 000
TEBA-Cl	5	63	4.85[c]	>15 000
TEBA-Cl	35	55	2.00	>15 000
$Bu_4N{\cdot}HSO_4$	5	51	0.36	~2700
$Bu_4N{\cdot}HSO_4$	5	59	0.28	<1000
$Bu_4N{\cdot}HSO_4$	35	65	1.80	>14 000
$Ph_4P{\cdot}Cl$	5	50	0.26	~2400
$Ph_4P{\cdot}Cl$	35	67	0.40	~6500

[a] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [b] Masses where the peaks of cyclic and linear polycarbonates display equal intensities. [c] SEC measurement with triple detection gave: $M_n \approx 215\ 000$ Da, $M_w \approx 620\ 000$ Da.

With respect to molecular weight and formation of cyclic polycarbonates, the four catalysts gave significantly different results. The highest number average molecular weights (M_n) of 215 × 10^3 g/mol and weight average (M_w) of 600 × 10^3 g/mol were obtained with TEBA. However, lower temperatures and high feed ratios of TEBA proved to be favorable for both high molecular weights and high fractions of cycle oligomers. MALDI-TOF analysis proved that most PTC catalysts performed rather poorly because they inefficiently hydrolyzed the chloroformate groups under such conditions (Table 6). Efficient chain growth and cyclization required 50% of the chloroformate groups to be hydrolyzed. Apparently, the transport of OH^- ions into the organic phase was inefficient, and was thus the rate-determining step.

In order to solve this problem the synthesis strategy was changed, and polycarbonates were obtained by the reaction of bisphenol A (BPA) and bisphenol C (i.e., [2,2-bis(*p*-hydroxyphenyl),-1,-1-dichloroethylene]) (BPC) with the bischloroformate of bisphenol A and bischloroformate of bisphenol C in the presence of DMSO as a catalyst (Figure 9).[24]

This research used various quantities of monomers and different monomer combinations. In the general procedure, NaOH (0.981 g) was dissolved in 50 mL of deionised water and added to a round-bottomed flask (750 mL), equipped with a reflux condenser, dropping funnel, and stirrer. Then the reactor was charged with the appropriate amounts of the monomers comprising BPA or BPC. The mixture was stirred while adding the required amount of the catalyst solution which was prepared by dropping dimethylsulfoxide (0.55 mL) into deionised water (50 mL). This catalyst solution was then introduced into the reactor. A further solution of CH_2Cl_2 (130 mL as the solvent)

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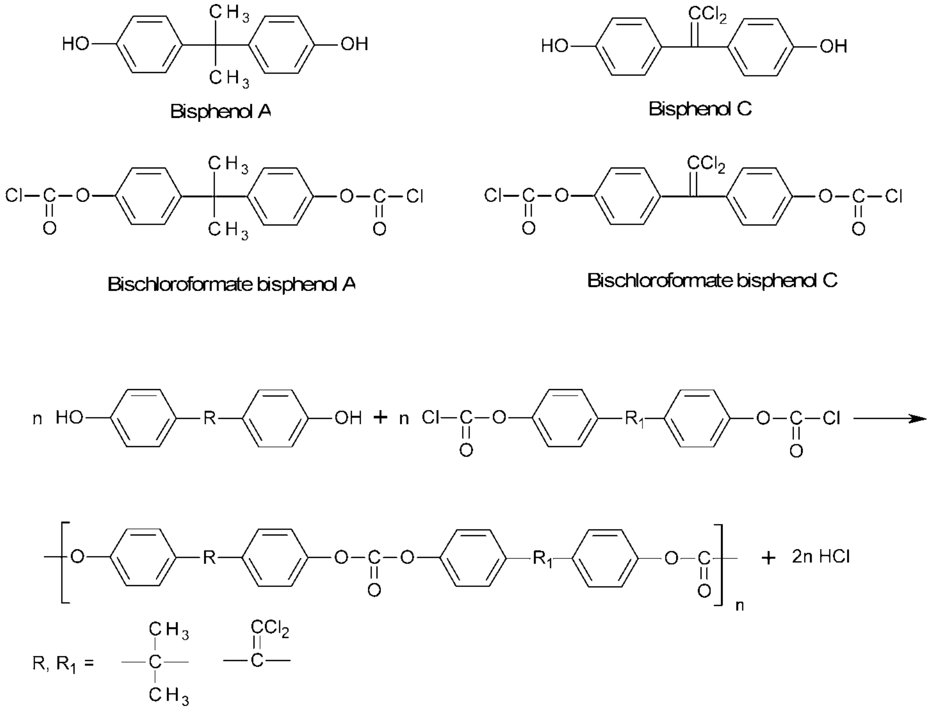

Figure 9. **Preparation of polycarbonates from bisphenol chloroformates.**

and the second monomer, bischloroformate of BPA or BPC, was prepared in a conical flask (250 mL). Then, the solution of the second monomer and solvent was added to the reactor. To get desired molecular weights of PC products, phenol (0.0375 g) was added in 30 min after the reaction completion. After separation of the water layer, the organic layer (with the product) was washed with deionised water (2 × 800 mL) with 10 min mixing each time. Finally, the product was precipitated by adding the organic layer very slowly to acetone (1 L) and collected in a vacuum sintered glass funnel filter. The product was then dried at room temperature. The optimum volume of the organic phase was 100−160 mol % that of the water phase. There was insufficient separation of the organic and aqueous layers when the lower volume was used. DMSO optimum amount was 80−120 mol % of the quantities of the monomers. The viscosity measurements indicate that the final polycarbonates were suitable for injection molding.

In the next paper, bisphenol A was polycondensed with diphosgene under PTC conditions to yield high-molecular-weight polycarbonates containing large fractions of cyclic polycarbonates.[25] Five of the following catalysts were examined: triethylamine, 4-(*N*,*N*-dimethylamino)pyridine (DMAP), ethyldiisopropylamine, (EDPA), tetrabutylammonium hydrogen sulfate (TBAHS), and triethylbenzylammonium chloride (TEBA). In a standard procedure, diphosgene (16 mmol) was dissolved in dry CH_2Cl_2 (200 mL) and cooled to 5−6 °C. BPA (20 mmol) was dissolved in water (200 mL) containing NaOH (64 mmol) and cooled to 5−6 °C. Then a catalyst (2 mmol) was added to the aqueous solution immediately before the polycondensation began. Both solutions were mixed at once and stirred with a high-speed stirrer for 10 min under cooling with an ice/NaCl mixture. The reaction mixture was then stirred for 50 min more with a flat-blade stirrer (several hundreds of revolutions per minute). Finally, the CH_2Cl_2 solution was separated from the aqueous phase after dilution with more CH_2Cl_2 and precipitated into methanol (Table 7).

Table 7. **Phosgenation of bisphenol A with diphosgene catalyzed with triethylamine: variation of the diphosgene/bisphenol A ratio**

$(COCl_2)$/ (BPA)	(NaOH)/ (BPA)	time (h)	yield (%)	η_{inh}[b] (dL/g)	M_{ei}[c]
20/20	40/20	1.0	69	0.21	2500
22/20	44/20	1.0	69	0.48	3800
24/20	48/20	1.0	71	0.56	4200
28/20	56/20	1.0	74	0.73	6000
32/20	64/20	1.0	83	0.80	6500
40/20	80/20	1.0	78	0.35	3000
40/20	80/20	0.5	74	0.32	–
40/20	80/20	2.0	81	0.36	–
40/20	80/20	4.0	79	0.36	–

[a] The feed ratios are given in millimoles. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] Mass at which the peaks of cycles and linear chains exhibit equal intensities in the MALDI-TOF mass spectrum.

It was found that EDPA underwent intensive side reactions with diphosgene so that only low-molecular-weight products are formed in the direct phosgenation of BPA. More nucleophilic *tert*-amines such as DMAP or triethylamine also specifically react with diphosgene, catalyzing rapid hydrolysis at the expense of chain growth and cyclization; thus, low feed ratios of DMAP and triethylamine are advantageous in the polycondensation. However, the molecular weights with higher concentrations of tetraalkylammonium salts (i.e., TBAHS or TEBA) increase because these catalysts favor chain growth in the organic phase via "naked" phenoxide ions without catalyzing the hydrolysis of diphosgene.

Polyamides. Recently, an interesting example of the synthesis of aromatic polyamides under PTC conditions was

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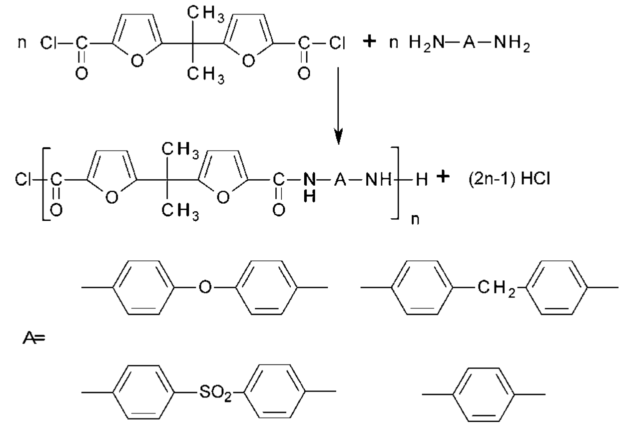

Figure 10. **General pathway for the synthesis of polyamides.**

Table 8. **Influence of the nature of the PTC catalyst on the interfacial synthesis of polyamide from diamine and furfural diacid chlorides**[a]

PTC[b]	TEBAC	TBAB	TBAS	HTAB	none
yield (%)	98	95	83	52	33
η_{inh} (dL/g)	0.25	0.223	0.162	0.086	0.045

[a] Reaction conditions: $V_{C_2H_2Cl_4}$ = 25 mL; V_{H_2O} = 6 mL; T = 80 °C; time = 3 h; **1**: 3.50 mmol; **2a**: 3.7 mmol; **NaOH**: 31.3 mmol; **PTC**: 0.12 mmol. [b] TEBAC = triethylbenzylammonium chloride; TBAB = tetrabutylammonium bromide, TBAS = tetrabutylammonium bisulfate; HTBA = hexadecyltrimethylammonium bromide.

described.[26] Furfural derivatives represent the first building block (Figure 10), which are readily available from a simple chemical treatment of a variety of agricultural and forestry byproducts.

In a general procedure, 3.7 mmol of diamine and 0.12 mmol of a PTC catalyst were dissolved in 6 mL of a 6 M aqueous NaOH solution in a 100-mL capacity blender, before adding, under vigorous stirring, a solution of 3.5 mmol of diacid chloride in 25 mL of an organic solvent. The reaction mixture was then kept under agitation (700 rpm) at 10−80 °C for 1−8 h after which it was poured into 150 mL of water. The precipitated polymer was isolated by suction filtration before being vacuum dried. All the syntheses were conducted with benzyltriethylammonim chloride (TEBA) as catalyst and compared to syntheses with other catalysts (Table 8). TEBA clearly displayed the best catalytic activity, albeit with only a minor improvement with respect to TBAB. It was also shown unambiguously that the presence of such a PTC agent is indispensable, since in its absence the performance of the polycondensation reaction was particularly poor.

Polyethers. Synthesis of a polyether by phase-transfer catalysis (PTC) was investigated for the reaction of 3,3-bis(chloromethyl)oxetane (BCMO) and various bisphenols (i.e., bisphenol A, 4,4-dihydroxyazobenzene, 4,4-dihydroxybiphenyl, 4,4-dihydroxybenzophenone, and 4,4-thiodiphenyl) (Figure 11).[27] The reactions were run under microwave irradiation according to the protocol: a mixture of bisphenol (1.3 mmol), water (5 mL), NaOH (3 g), nitrobenzene (5 mL), BCMO (1.3 mmol), and TBAB (0.2 mmol) was placed in a 50-mL flask and irradiated for 1.5 h in a microwave waveguide (60 W).

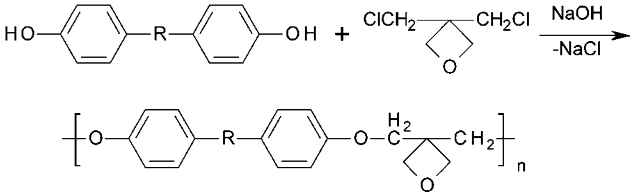

Figure 11. **Synthesis of polyethers by phase-transfer catalysis (PTC) reactions.**

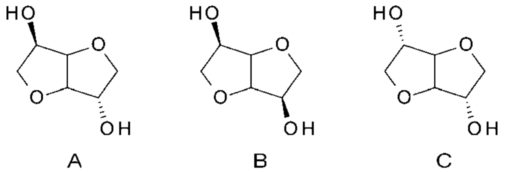

Figure 12. **(A) Isosorbide (1,4-dianhydro-D-sorbitol), (B) isomannide (1,4-dianhydro-D-mannitol), (C) isoidide (1,4-dianhydro-D-iditol).**

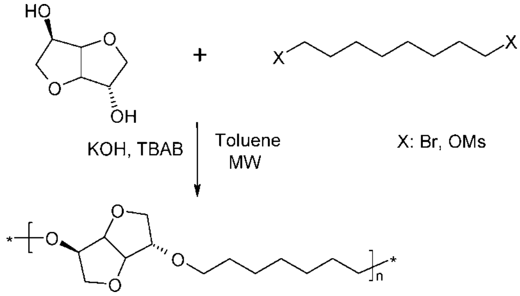

Figure 13. **Synthesis of linear polyethers from either isosorbide or isoidide and disubstituted alkyl bromides or methanesulfates.**

The temperature (95−100 °C) was monitored by a thermovision infrared camera. Under conventional conditions, the reaction required 5 h at 90 °C. It was found that in the case of semicrystalline polyethers, the yields were higher under microwave conditions, whereas in the case of amorphous polyethers, the yields were approximately equal although requiring a shorter reaction time.

By using microwave protocol under solid−liquid PTC conditions, the synthesis of linear polyethers from either isosorbide or isoidide and disubstituted alkyl bromides or methanesulfates was also described (Figure 12).[28,29] Isosorbide and isoidide (Figure 12) are obtained from the byproducts of biomass (i.e., sugar industry) through double dehydration of starch as byproducts.[30]

The reactions were carried out in a microwave reactor with temperature infrared detector. Typically, the reaction mixtures consisted of isosorbide or isoidide (5 mmol), and alkylene dibromide/dimethanesulfate (5 mmol), tetrabutylammonium bromide (TBAB, 1.25 mmol), and powdered KOH (12.5 mmol) were irradiated for 30 min to afford the polyethers with 70−90% yield (Figure 13).

In the case of isosorbide, the microwave-assisted synthesis proceeded more rapidly (30 min) as compared with conventional heating. The yield was 69−78% as compared to 28−30 under

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Table 9. **Influence of reaction time on the yields of high-molecular-weight fraction (FP MeOH) and low-molecular-weight fraction (FP Hex) of polyethers**

time	mode of activation[a]	FP MeOH (%)	FP Hex (%)	total yield (%)
30 min	MW	67	18	85
60 min	MW	71	19	90
30 min	Δ	12	81	93
1 day	Δ	64	25	89
1 week	Δ	83	5	88
1 month	Δ	91	0	91

[a] MW - microwave irradiation; Δ - conventional thermal heating.

conventional conditions. Similar yields of the polyethers were obtained when the reaction time was extended to 24 h. These yields remained practically unchanged even though the synthesis was carried out for another 7 days (Table 9).

The analysis of properties of the synthesized polyethers revealed that the structure of the products strictly depended on the activation mode (i.e., microwave or conventional activation). Polyethers were characterized by higher molecular weights when prepared under microwave heating conditions. In turn, within 30 minunder conventional heating, the higher molecular weight polyethers were not observed at all. Moreover, it was found that the mechanism of chain termination is different under microwave and conventional conditions. The polyethers prepared with conventional heating have shorter chains with terminal hydroxyl ends, whereas under microwave irradiation the polymer chains were longer with terminal ethylenic ends.[28]

Recently, the same experimental conditions were applied to the polycondensation of aliphatic diols of isosorbide with 1,8-dimesyloctane and other dibromo- and disulfonated alkylating agents (Figure 14).[31]

In all the cases, it was found that microwave-assisted polycondensations proceeded more efficiently compared with conventional heating (the reaction time was reduced from 24 to to 30 min). The polycondensation under microwave yields 63% of polyethers with relatively high weight average molecular weights up to 7000 g/mol. It was demonstrated that the application of previously synthesized ethers of isosorbide was beneficial and allowed preparation of polyethers in better yields than the polyethers obtained in direct reactions of isosorbide and dibromo- or dimesylalkenes. Moreover, the molecular weights of the polyethers were higher than of those prepared in the earlier work, while molecular weight distributions of new polyethers were similar or lower. Such a microwave-assisted procedure can contribute to synthesis of alternating polyethers and further modification of their properties. Some conclusions (i.e., shorter reaction time, higher molecular weight, and structure of polymers) for the polycondensation reactions when compared under microwave and conventional heating conditions have previously been noted:[31]

- to an increase in system polarity from the ground state (GS) of the reaction, which consists of tight ion pairs (involving hard alkoxide anions) toward the transition where ion pairs are much looser due to negative charge delocalization; it results in an enhancement in polarity during the reaction progress and, consequently, to an increase of microwave materials interactions magnitude responsible for the observed acceleration
- to some dipole orientation influence in the presence of an electromagnetic field that could induce some mutual special orientation of reagents
- to enhanced microwave stabilization by dipole−dipole interaction of the more polar transition state (TS); in elimination TS, to a greater delocalization of negative charge compared with substitution TS, polarity is enhanced in connection with a looser ion pair.

Poly(*p*-phenylene oxide). Owing to their resistance to high temperatures and a very high glass transition temperature (i.e., ∼210 °C), poly(*p*-phenylene oxide) (PPO) has become a high-performance polymer and an engineering thermoplastic. There are two well-established approaches to the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers. One consists of the polymerization of 2,6-dimethylphenol in the presence of a copper−amine complex catalyst. A radical−radical coupling mechanism is believed for this polymerization. The second synthesis is based on a radical anion polymerization of 4-bromo-2,6-dimethylphenol under both PTC and biphasic reaction conditions. Recently, it was demonstrated that the PTC polymerization of 4-bromo-2,6-dimethylphenol in the presence of

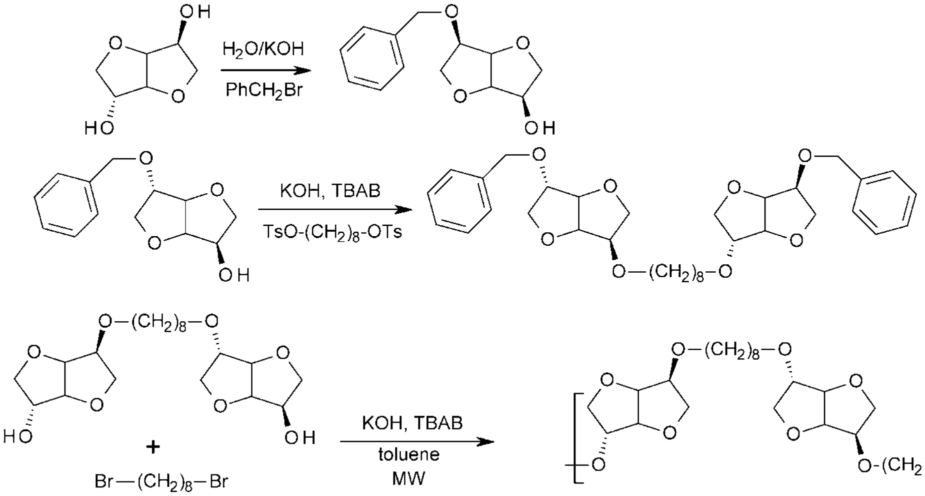

Figure 14. **Polycondensation of aliphatic diols of isosorbide with 1,8-dimesyloctane and other dibromo- and disulfonated alkylating.**

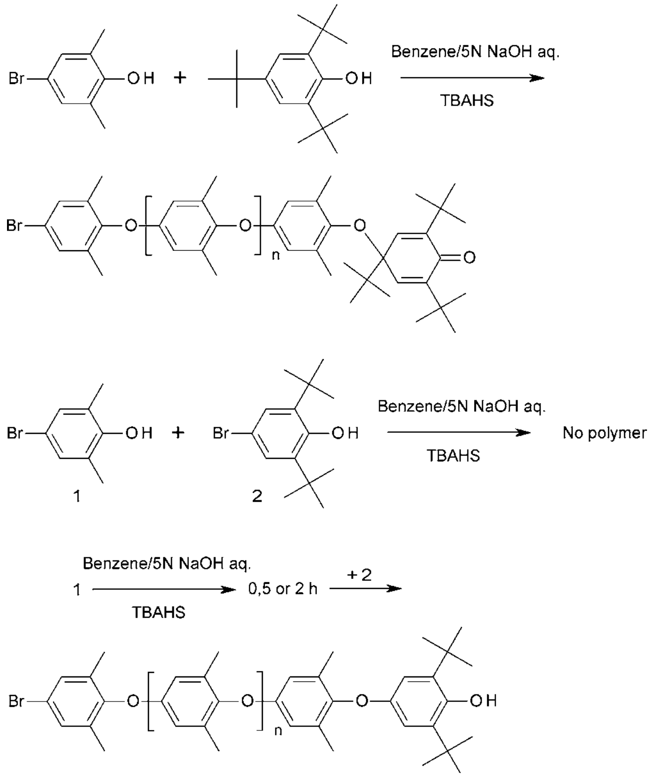

Figure 15. **Preparation of poly(*p*-phenylene oxide) (PPO).**

either 2,4,6-trimethylphenol or 4-*tert*-butyl-2,6-dimethylphenol was a novel technique to synthesize PPO with controllable molecular weights (Figure 15).[32]

Polymerization experiments were performed in a PTC system (i.e., benzene/1.5 N NaOH (aq)) with tetrabutylammonium hydrogen sulfate (TBAHS) or tricaprylmethylammonium chloride (Aliquat 336) catalysts. In a typical polymerization experiment, 4-bromo-2,6-dimethylphenol (5.00 g, 24.9 mmol) was added to a solution of 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (1.77 g, 6.22 mol) in 50 mL of 1.5 N aqueous NaOH. Then 50 mL of benzene and TBAHS (0.422 g, 1.24 mmol) were added to the reaction mixture. The reaction was stirred for 24 h at 25 °C. Next, the benzene layer was precipitated into methanol. The results of the polymerization experiments are listed in Table 10. Polymerization experiments were run with 1/2 molar ratios of 4/1, resulting in PPO-2OH with M_n of 2200−3200 g/mol; however, the polymer yield was 14−25% presumably due to the fact that lower-molecular-weight PPO-2OH oligomers are soluble in methanol and therefore are lost during the precipitation process.[33]

Poly(etherketone)s and Poly(etherimide)s. Aromatic poly(etherketone)s are useful as high-performance engineering thermoplastics. A novel synthetic method for the preparation of high-molecular-weight aromatic poly(ether ketone)s was described, in which *N*-alkyl(4-*N*′,*N*′-dialkylamino)pyridinium chlorides were used as PTC catalysts.[34] A general procedure involved mixing 50 mmol bisphenol, 50 mmol of 1,4-bis(4-chlorobenzoyl)benzene, 150 mmol anhydrous K_2CO_3, and 0−5 mmol PTC catalyst in a 250-mL flask equipped with a mechanical stirrer, a water separator, and an addition funnel. Then, dimethylacetamide (DMAc) (100−120 mL) and toluene (40 mL) were added dropwise. The stirred mixture was then heated under argon to 60 °C. Then, the mixture was heated to 155 °C for 3 h while the toluene−water azeotrope was removed by distillation. Finally, the polymer was then precipated by pouring the hot solution slowly into a blender containing a water/acetic acid mixture (Figure 16).

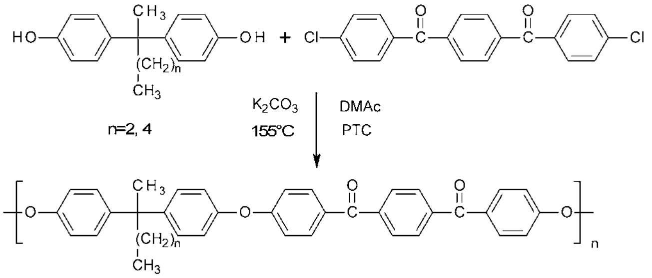

Figure 16. **Preparation of aromatic polyethers.**

High-molecular-weight amorphous poly(ether ketone)s were obtained which exhibited excellent solubility in CH_3Cl, CH_2Cl_2, and THF. The polymer was also obtained by condensation in the absence of PTC catalysts (M_w > 100 000 g/mol), but the reaction time increased to 17 h. With PTC (5 mol % relative to the monomer amount), high-molecular-weight products (M_w >170 000 g/mol) are formed within 7 h. Furthermore, the catalyzed reactions result in material of higher molecular weight than do the uncatalyzed reactions (Table 11).

The synthesis of poly(ether imide)s in the condensation of disodium salt of bisphenol A and bis(chlorophthalimide)s in *o*-dichlorobenzene solution under microwave irradiation was also described (Figure 17).[35] For this purpose, 16.12 mmol of bis(chlorophthalimide)s and 16.12 mmol of disodium salt of bisphenol A in 60 mL of *o*-dichlorobenzene with 0.56 mmol of hexaethylguanidinium bromide were irradiated in a domestic microwave oven for 25 min and precipitated from methanol. The polymerization reactions, in comparison with conventional heating polycondensation, proceeded rapidly (25 min vs 4 h at 200 °C), and the polymers with inherent viscosities in the range of 0.55−0.90 dL/g were obtained.

Epoxy Resins. Industrial methods for the synthesis of epoxy resins are based on the two-step reaction of halohydrins with

Table 10. **Polymerization of 4-bromo-2,6-dimethylphenol (1) and 2,2-di(4-hydroxy-3,5-dimethylphenyl)propane (2) under PTC conditions**

1 (mmol)	**2** (mmol)	**1**/**2** (mmol)	phase transfer catalyst	reaction time (h)	polymer yield (%)	M_n SEC (g/mol)	$(M_w)/(M_n)$
24.9	6.22	4/1	TBAH	24	25	2700	1.43
24.9	6.22	4/1	TBAH	12	17	3200	1.41
4.98	1.24	4/1	TBAH	24	16	2600	1.22
4.98	1.24	4/1	Aliquat 336[a]	24	19	2200	1.22
4.98	1.24	4/1	TBAH	12	14	3000	1.41

[a] Tricaprylmethylammonium chloride.

Table 11. **Conditions and results for poly(ether ketone) synthesis under PTC conditions**[a]

monomers:[b] dihalide/ bisphenol	PTC catalyst	amount of catalyst (%)[a]	reaction time (h)	M_w (g/mol)
A/B	uncatalyzed	–	17.00	124 200
A/C	uncatalyzed	–	17.50	120 900
A/B	1	5	7.00	174 200
A/B	1	10	4.50	192 700
A/C	2	10	5.00	196 000
A/C	3	10	4.50	202 300
D/B	–	–	2.00	225 500
D/C	–	–	1.75	232 100

[a] Related to the amount of monomers; where: **1** = *N*-neopentyl(4-dibutyloamino)pyridynium chloride, **2** = *N*-neopentyl(4-dihexyloamino)pyridinium chloride, **3** = *N*-neopentyl-4(4′-methylpiperidinylene)pyridinium chloride. [b] A = 1,4-bis(4-chlorobenzoyl)benzene, B = 2,2′-bis(4-hydroxyphenyl)pentane, C = 2,2′-bis(4-hydroxyphenyl)heptane, D = 1,4- bis(4-fluorobenzoyl)benzene.

bifunctional phenol or alcohols. The first step, catalyzed by NaOH, is the addition reaction of epichlorohydrin to bisphenol A via the opening of the epoxy ring. In the second step, hydrogen chloride is extruded, and the epoxy ring is reconstructed (Figure 18). Polymers grow by the repetition of this sequence. Recently, PTC conditions were applied for the synthesis of low-molecular-weight epoxy resins in a single-stage process, in the presence of ammonium salts (i.e., triethylbenzyl-, trioctylbenzyl-, tributylbenzylammonium chlorides as well as cetyltrimethylammonium bromide) and/or sulfoxides and sulfolanes as catalysts.[36]

In a general procedure, a 500 mL flask equipped with an efficient stirrer and a dropping funel was charged with CH_2Cl_2 (200 mL), a catalyst (2−10 wt %), bisphenol A (22.8 g, 0.1 mol), and epichlorohydrin (33 mL, 0.3 mol). Then, a concentrated (50%) aqueous solution of NaOH (8 g, 0.2 mol) was added dropwise within 2 h at room temperature. After introduction of the whole amount of NaOH, stirring was continued for 2 h. Finally, the reaction was stopped by an addition of water, and the organic phase was separated. The excess of epichlorohydrin and organic solvent was distilled off to give 26.5 g of epoxy resin. It was found that the optimum reaction conditions for obtaining the low-molecular-weight epoxy resins were a two-phase system, CH_2Cl_2/50% aqueous solution of NaOH, and a molar ratio of bisphenol A/epichlorohydrin/NaOH, 1:3:2. Under these conditions, a number of quaternary ammonium salts and sulfoxides/sulfolanes were tested. Trioctylbenzylammonium chloride and dibutyl sulfoxide were the most effective catalysts, giving resins with the highest values of epoxy equivalent and lowest polydispersity (Table 12).

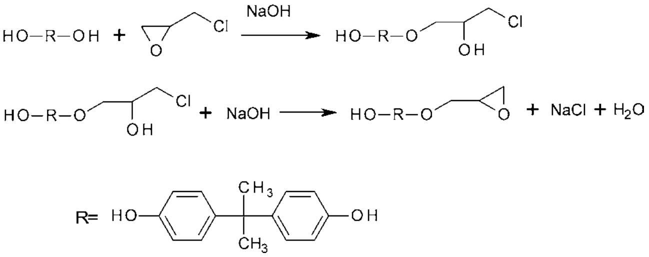

Figure 18. **Pathway of the reaction of bisphenol A and epichlorohydrin.**

Table 12. **Catalysts, yields, and properties of the low-molecular-weight epoxy resins synthesized from bisphenol A and epichlorohydrin under PTC conditions**

PTC catalyst	$M_{n(g/mol)}$	$M_{w(g/mol)}$	P_d	epoxy equivalent[a]
triethylbenzylammonium chloride	453	621	1.37	0.447
cetyltrimethylammonium bromide	576	1425	2.47	0.348
methyltrioctylammonium chloride	560	832	1.49	0.354
trioctylbenzylammonium chloride	364	455	1.25	0.553
tributylbenzylammonium chloride	608	801	1.32	0.333
dimethylsulfoxide	380	410	1.08	0.506
diphenylsulfoxide	506	532	1.05	0.383
dibuty lsulfoxide	366	385	1.05	0.531
sulfolane	431	430	1.06	0.458
2,4-dimethylsulfolane	375	1142	3.04	0.513
dimethylsulfone	584	1689	2.89	0.327
diphenylsulfone	540	906	1.68	0.361
commercial product: “Epidian 6”	349	404	1.16	0.545

[a] Determination of the epoxy group equivalent was carried out according to PN-87/C-89085/13.

The synthesis of high-molecular-weight (solid) epoxy resins under PTC conditions was also described.[37,38] The method was based on the polyaddition of bisphenol A to a low-molecular-weight epoxy resin or bisphenol A diglycidyl ether (DGEBA) in the presence of ammonium salts, phosphonium salts, and imidazole derivatives as a catalyst (Figure 19).

The syntheses were performed under microwave irradiation and conventional thermal heating (i.e., electric heating mantle) for the comparison of the properties of high-molecular-weight epoxy resins formed under both conditions. All the reactions were carried out in a 250-mL flask charged with 11.6 g of bisphenol A, 25.0 g of low-molecular-weight epoxy resin (epoxy value = 0.57

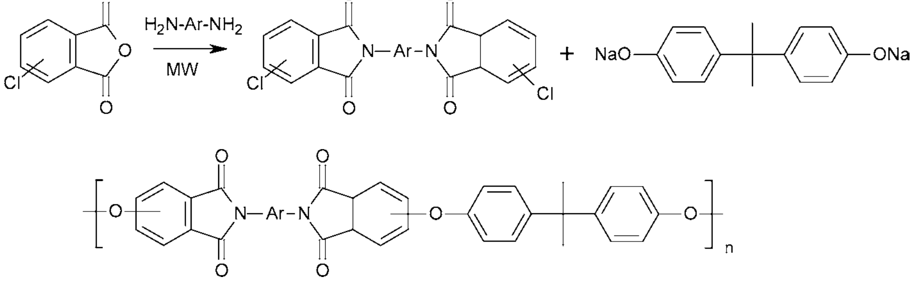

Figure 17. **Polycondensation of disodium salt of bisphenol A and bis(chlorophthalimide)s.**

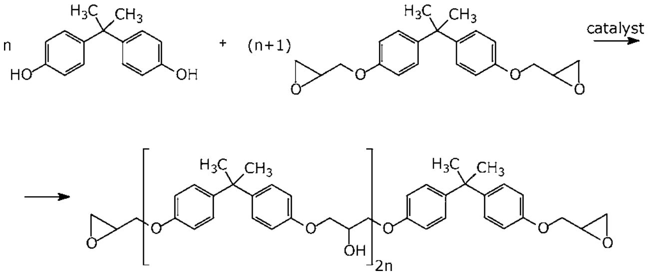

Figure 19. **Preparation of high-molecular-weight epoxy resins.**

mol/100 g), and a small amount of a catalyst. For microwave experiments, the flask was irradiated in a multimode microwave reactor with maximum power of 600 W. The main advantage of the microwave process is a 2-fold reduction of reaction time in comparison to that of conventional conditions. The molecular weight distribution and degree of branching of the solid epoxy resins synthesized under microwave irradiation were comparable with those obtained under conventional heating and were not influenced by the reduction in reaction time (Table 13).[38]

The surface temperatures of the solid epoxy resins samples were monitored during formation by means of the thermovision camera in order to compare the temperature distribution under microwave and conventional conditions for both stirred and nonstirred reaction mixtures (Figure 20).

The experiments were carried out at 160 °C, and as was expected for an exothermic reaction, the highest temperatures were observed in the center of the reaction vessel for all the processes (Figure 20a−d). Furthermore, for both microwave and conventional processes, the stirring of the reaction mixture resulted in more uniform temperate profiles (Figure 20a,c), respectively, while for the nonstirred reaction mixture, the maximum surface temperature under microwave irradiation was much higher (approximately 200 °C) than the average bulk temperature of reaction mixture. Moreover, for the nonstirred samples prepared under microwave irradiation, high temperature heterogeneity was observed (Figure 20b), which, in turn, led to cross-linking of resins. Under conventional conditions, the temperature for the nonstirred reaction mixture was more inhomogeneous then for the stirred mixture, but the maximum surface temperature reached only 170 °C (Figure 20d). Finally, it was found that the uncured as well as cured high-molecular-weight epoxy resins have good thermal stability up to 370 and 360 °C, respectively, at which point the degradation of the samples in an air atmosphere occurred for ∼5% of the samples.[37]

Lately, the same approach was used for the synthesis of solid epoxy resins with reduced flammability.[39] For this purpose, bisphenol A was either substituted or partially substituted with 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (Figure 21), and the synthesis of solid epoxy resins was realized in the same manner as described previously.

Large-Scale Applications. Recently, the synthesis of high-molecular-weight (solid) epoxy resins from bisphenol A and a low-molecular-weight epoxy resin (Figure 19) in a continuous microwave reactor, that consists of four microwave cavities with a rotating quartz tube (2.0 m × 0.12 m), was tested in the presence of ammonium or phosphonium salts as well as imidazole derivatives as a catalyst (Figure 22).[40]

All the microwave cavities are equipped with a continuous power regulation and temperature control, while each magnetron can be separately switched on and off if necessary, which offers the advantage of reduced power consumption compared to continuous power control. The speed of the quartz tube rotation is also continuously adjustable. It was shown that by applying continuous microwave power it was possible to obtain high-molecular-weight epoxy resins with an epoxy value of 0.11 mol of epoxy group per 100 g of resin by maintaining at a flow of 8 kg/h. In one of the experiments, the product (epoxy resin) was not removed from the reactor, and the resin samples were taken from different parts of the tube and

Table 13. **Reaction conditions and properties of solid epoxy resins**

conditions[a]	temp. (°C)	catalyst content (mol × 10^3)	time (min)	epoxy value (mol/100 g)	M_n (g/mol)	SEC M_w (g/mol)	P_d
mv	140	0.5	150	0.114	1810	3260	1.80
		1.0	90	0.112	1470	2580	1.75
		5.0	25	0.110	1950	3780	1.94
mv	160	0.5	65	0.110	2140	3780	1.77
		1.0	40	0.113	1850	3390	1.83
		5.0	20	0.104	2470	3390	1.83
mv	180	0.5	65	0.109	2380	4340	1.85
		1.0	30	0.109	2180	3990	1.83
		5.0	16	0.105	2420	4580	1.89
Δ	140	0.5	280	0.114	1380	2860	2.08
		1.0	150	0.114	2020	3760	1.86
		5.0	55	0.113	2170	3640	1.68
Δ	160	0.5	120	0.106	1790	3130	1.75
		1.0	80	0.111	2180	4000	1.84
		5.0	35	0.100	2380	5010	2.10
Δ	180	0.5	80	0.101	2180	4000	1.84
		1.0	50	0.105	2250	4250	1.89
		5.0	35	0.100	2320	4420	1.91

[a] MW-microwave irradiation, Δ-conventional heating (i.e., electric heating mantle).

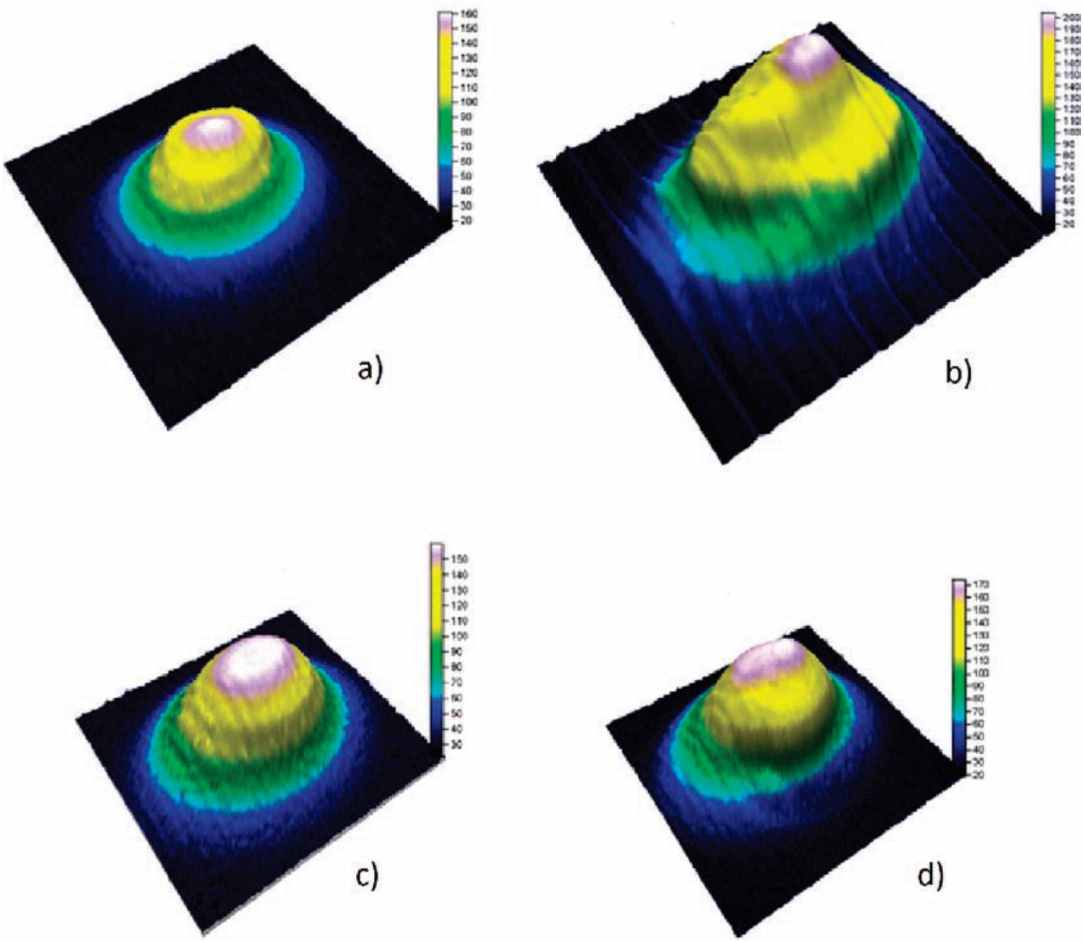

Figure 20. **Surface temperature of the solid epoxy resins samples monitored by means of the thermovision camera.**

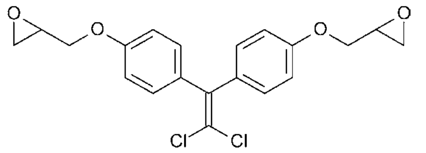

Figure 21. **1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethylene.**

Figure 22. **Continuous microwave reactor with rotating quartz tube for the synthesis of high-molecular-weight epoxy resin (Ertec, Poland).**

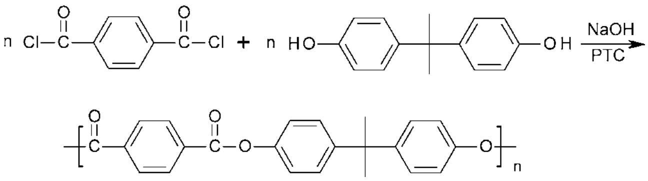

Figure 23. **Preparation of polyarylates from isophthaloyl and terephthaloyl chlorides and bisphenol A.**

analyzed for the conversion i.e. epoxy values. The planned epoxy value (i.e., 0.11 mol/100 g) was reached in the middle of the tube, which means that the reactor can even work at higher flow rates than 8 kg/h.[40]

More recently, a continuous Taylor−Couette reactor for the polycondensation of bisphenol A with terephthaloyl and isophthaloyl chlorides under the PTC conditions was reported (Figure 23).[6]

In a general procedure, the solutions of bisphenol A, TEBA, NaOH in water (TA-1) and terephthaloyl and isophthaloyl

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Table 14. **Range of experimental parameters for polycondensation of bisphenol A and terephthaloyl and isophthaloyl chlorides in a continuous Taylor−Couette reactor**

initial concentration of bisphenol A in aqueous phase, C°_{BPA} (mol/dm^3)	0.054; 0.108
concentration of NaOH in aqueous phase, C_{NaOH} (mol/dm^3)	0.156; 0.312
concentration of TEBAC in aqueous phase, C_{TEBAC} (mol/dm^3)	6.585×10^{-3}
concentration of mixture iso- and terephthaloyl chlorides, $C_{\mathrm{I+T}}$ (mol/dm^3)	0.042−0.115
concentrations ratio of terephthaloyl chloride to isophthaloyl chloride (mol/dm^3)	2.1
rotation speed, N (rpm)	500−2500
residence time, t (s)	20−60
annular gap width, d (mm)	1.5−5
volumetric aqueous phase flow rate, Q_{Aq} (mL/min)	20−107
volumetric organic phase flow rate, Q_{Org} (mL/min)	26−126
volume fraction dispersed (organic) phase, ϕ (no units)	0.24−0.74
temperature, T (°C)	5−20

chlorides in CH_2Cl_2 (TA-2) were put into separate tanks and then poured into the reactor, where polycondensation followed (Table 14).

After stabilizing of the process parameters (temperature, rotational speed of the rotor, solutions flow rates and volumetric flow ratio of organic to aqueous phase), samples were withdrawn, phase separation took place, and acetone was added to a CH_2Cl_2 solution in order to precipitate the polymer (Figure 24). Next the solution was filtered, and the obtained polyarylates were dried at room temperature for a few days.

The results of the process carried out in this type of a continuous reactor were considered in terms of the influence of the initial monomer's molar ratio M_0 on the properties of the polyarylate (i.e., the average molecular weight, MW, and polydispersity index, PI). It was shown that they can be interpreted if two factors are considered. For molar ratios of $M_0 > 1.2$, the influence of both monomer's molar ratio and mixing intensity (the hydrodynamics of the TCR) was not significant on the final properties of the polyarylates. The molecular weight and the polydispersity index maintain constant values 3000 g/mol and 1.6, respectively. In the second one, for the molar ratio $M_0 < 1.2$, a significant influence of the monomer's molar ratio M_0 and intensity of mixing on the properties of the product was observed. Additionally, in this region the impact of parameters such as the process temperature, the mixture flow rate and the annular gap width has become evident. Moreover, the possibility of obtaining a product displaying desirable properties suitable for the production of fibers or polymeric films was proved. A product of desirable properties can be obtained for the following ranges of the process parameters: $0.7 < M_0 < 0.9$ and $1210 \leq \mathrm{Rerot} \leq 1400$ for $t = 20$ °C, $\tau = 60$ s, and $\eta = 0.93$ (where Rerot = rotational Reynolds number, τ = residence time, and η = ratio of the inner and outer cylinder diameter of the reactor). Considerably, shorter residence times, of the order $\tau = 60$ s, can be reached in the Taylor−Couette reactor in comparison with the reaction times in the stirred-tank-reactor, of the order $\tau = 300{-}600$ s, depending on the monomer's molar ratio, M_0.

Conclusion

PTC creates clean, selective and efficient conditions for performing a number of polycondensation reactions with attributes of mild conditions and simplicity. Significant improvements in the yields of PTC-catalyzed reactions and/or reaction conditions can be generally achieved, together with considerable simplification of operating procedures. A number of PT-catalyzed polycondensation reactions can be scaled from small-scale synthesis (grams) up to multigram level (100−300 g) and sometimes kilogram level protocols. Examples cited in this paper related to PTC protocols include:

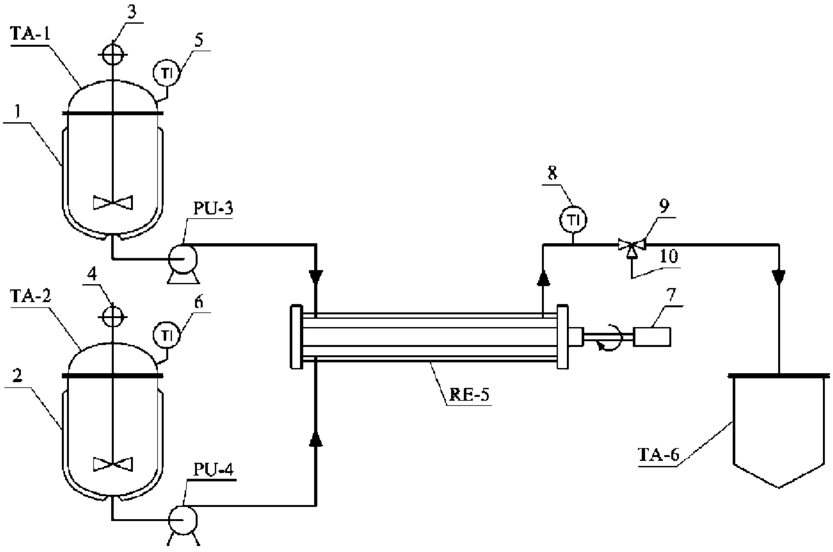

Figure 24. **Experimental setup: (TA-1) tank with aqueous phase; (TA-2) tank with organic phase; (PU-3, PU-4) peristaltic pumps; (RE-5) TCR; (TA-6) tank with outlet mixture; (1 and 2) cooling jackets; (3 and 4) stirrers; (5, 6, and 8) thermometers; (7) motor and control device; (9) three-way valve; (10) the sampling point.**

- preparation of poly(etherketone)s and poly(etherimide)s 20−30 g[34,35]
- synthesis of low-molecular-weight epoxy resins 30 g[36]
- preparation of polyarylates 140 g,[20]
- synthesis of high-molecular-weight epoxy resins 30−8000 g[37,38,40]
- preparation of polyarylates in Taylor−Couette reactor 500−4000 g.[6]

In the future, the application of PTC to polymer chemistry will lead to faster and cleaner reactions when compared to conventional protocols. Solvent can often be excluded from the reaction when the electrophile is a liquid and therefore act both as a reagent and the organic phase. The possible acceleration of such reactions might be optimum, because they are not moderated or impeded by solvents, which has an impact for green chemistry considerations.

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