

Zbigniew K. Brzozowski¹, Anna Stec² and Zbigniew Wielgosz²

NEW ROUTE FOR POLYCARBONATES

¹ Central Institute for Labour Protection, National Research Institute,
Warsaw University of Technology, Faculty of Chemistry,
Koszykowa 75, 00-662 Warsaw, Poland, zbigbi@ch.pw.edu.pl

² Uklan, School of Forensic and Investigative Sciences University of Central Lancashire, United Kings

³ Industrial Chemistry Research Institute, Poland

Received: October 15, 2008

© Brzozowski Z., Stec A., Wielgosz Z. 2009

Abstract. A new route for obtaining chemically pure and ecological polycarbonates has been developed. The process was carried out without any amines with dimethylsulfoxide (DMSO) as interfacial catalyst. It was established that DMSO was between 80–120 mol % to the quantities of applied monomers. Bisphenol A and bisphenol C [2,2-bis(*p*-hydroxyphenyl)-1,1-dichloroethylene] were applied as bisphenolic monomers

Key words: polycarbonates, dimethylsulfoxide (DMSO), interfacial catalyst, Bisphenol A, Bisphenol C.

1. Introduction

High transparency, outstanding impact strength, and ductility, superior dimensional stability, inherent fire resistance, good electrical properties, and thermal stability are some of the properties which make polycarbonate (PC) one of the most widely used thermoplastics compounds. Bisphenol A, by virtue of its low cost, good transparency and excellent mechanical properties is the major material used in polycarbonate processes where carbonate groups are linked together in a polymer chain.

Polycarbonates are commonly formed by the phosgenation of bisphenols, usually bisphenol A $[(CH_3)_2C(C_6H_4OH)_2]$, ester exchange between diaryl carbonates and bisphenols, usually between diphenyl carbonate $[(C_6H_5O)_2CO]$ and bisphenol A or interfacial polycondensation of phosgene and aromatic or aliphatic carbonate.

Polymers of high molecular weight using quaternary ammonium salts or triethylamine as the catalyst, and methylene chloride as the solvent, are currently obtained by an interfacial reaction (polycondensation) [1]. This is the dominant commercial process which requires strict temperature control because of the exothermic behaviour of the reaction and the boiling point of methylene chloride (313 K). The react product is a heterogenous mixture consisting of the polymer dissolved in an organic phase, *i.e.* aqueous and organic, which is subjected to further

processing [2-4]. Among the disadvantages, there is the possibility that triethylamine will react with bischloroformates or phosgene and, as a result, contribute to a partial hydrolysis [5, 6]. This will result in lower yields of PC and higher yields of unwanted products. There are also health and safety concerns connected with the use of phosgene in the interfacial process. $COCl_2$ as the reagent is highly toxic. Results for small scale experiments on the preparation of polycarbonates through the interfacial polycondensation of bisphenols with new catalyst as an alternative are presented.

Dimethyl sulfoxide (DMSO) was tested as the catalyst in polycarbonates replacing tertiary amine or quaternary ammonium salts. One of the advantages of this method is that the reaction proceeds at temperature between 278–298 K. Thus, there is no difficulty in keeping the reagents thermally stable (methylene chloride). In this process DMSO does not react with monomers whereas amine salt could react with phosgene or bischloroformates. Moreover, the PC product obtained from this new process generally contains very low level of impurities and exhibits outstanding stability under polymer processing conditions. The procedure without using $COCl_2$ and amines using monomers: bisphenol A, chlorobisphenol C and bischloroformates bisphenol A and C, and DMSO as catalyst is now presented.

In addition to describing the new route to chemically pure and ecological polycarbonates this paper is also a continuation of a new research on fire-safe polymers – chloral derivatives based on bisphenol C [2,2 bis(*p*-hydroxyphenyl) 1,1 dichloroethylene] and related halogen-containing compound [7-15].

2. Experimental

2.1. Materials

Bisphenol A [BPA 2,2-bis(4-hydroxyphenyl)propane] was commercially available from Blachownia Chemical Works (Poland). Bisphenol II (C)

[BPC 1,1-dichloro-2,2-bis(4-hydroxyphenyl)-ethylene] was synthesized in our lab according to the description [16–18]. Bischloroformates Bisphenol A and Bisphenol C were synthesized in the Institute of Industrial Organic Chemistry (Poland) (Fig. 1). Dimethyl sulfoxide (DMSO) was produced in POCH S.A. (Poland). Methylene chloride (CH_2Cl_2) was produced in Chempur (Poland).

2.2. Synthesis

Polycarbonates were synthesized from bisphenol A (BPA) or bisphenol C (BPC) and bischloroformate: bisphenol A or C. (Fig. 1).

This research used various quantities of monomers (Table 1) and different monomer combinations (Fig. 2); the general procedure is described below.

The reactor was a three-necked round-bottomed flask (750 cm^3), equipped with a reflux condenser, dropping funnel and stirrer. About 0.981 g sodium hydroxide was dissolved in 50 ml of deionised water. When NaOH was fully dissolved the reactor was charged with the appropriate amounts of the monomers comprising BPA

or BPC or the mixture of these two compounds. The mixture was stirred while adding the required amount of the catalyst solution which was prepared by dropping dimethyl sulfoxide (0.55 ml) into a second volume of deionised water (50 ml). This catalyst solution was then introduced into the reactor, after bisphenol A or C was fully dissolved using a dropping funnel. The stirring rate was then increased to 700 rpm (revolutions per minute) for the next 10 min. During stirring a further solution of dimethyl chloride (130 ml as the solvent) and appropriate amount of second monomer – bischloroformate BPA or BPC –was prepared in a conical flask (250 ml). After 10 min the stirrer in the reactor was adjusted to about 2000 rpm to ensure that the entire mixture (*i.e.* organic and aqueous phase) was fully homogenized. Then, the mixture of the second monomer and solvent was added to the reactor. These processes took 15 min. The point when the addition was completed was taken as the start of the reaction time.

To get desired molecular weight of PC products, phenol (0.0375 g) was added in 30 min after the reaction completion.

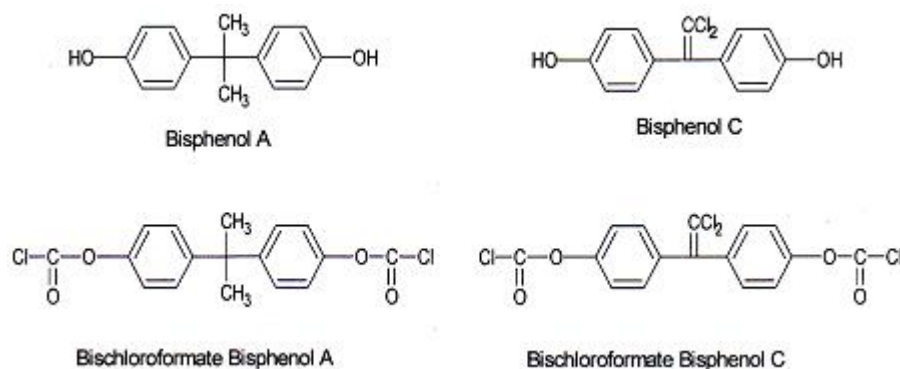


Fig. 1. Monomer structures

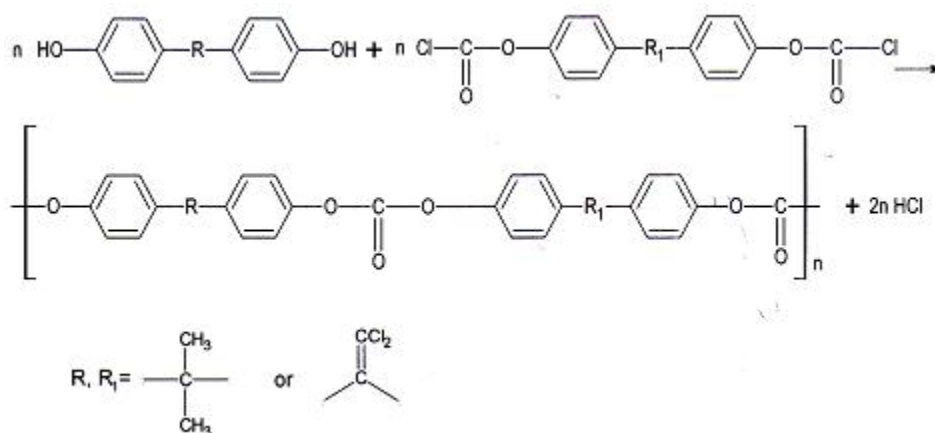


Fig. 2. Polycondensation reaction

Table 1

Various quantities of monomers and different monomer combinations

No	Bisphenol A, g	Bisphenol C, g	Bischloroformate Bisphenol A, g	Bischloroformate Bisphenol C, g
1	2.287		3.542	
2		2.811	3.542	
3	2.287			4.066
4		2.811		4.066
5	1.484 (65 mol %)	0.984 (35 mol %)	3.542	
6	0.800 (35 mol %)	1.827 (65 mol)	3.542	
7	1.484 (65% mol)	0.984 (35% mol)		4.066
8	0.800 (35% mol)	1.827 (65% mol)		4.066

When the reaction was complete the water phase was decanted. However, because of difficulties in the product isolating 100 ml of saturated saline solution can be added, which helps separate the organic phase from the aqueous layer. After separation of the water layer the organic layer (with the product) was washed twice with deionised water (800 ml) with 10 min mixing each time. Then the reaction product was acidified with sulfuric acid (800 ml deionised water plus 30 ml 50 % H_2SO_4) to reduce the pH of the reaction mixture. The process was continuously mixed until the organic phase containing the product was neutral. Finally, when the aqueous phase was decanted, the reaction product was washed a few times (30 min each) by 800 ml of deionised water to ensure that all traces of acid and other contaminants were removed.

The product was precipitated by adding very slowly to acetone (1 l), and collected in a vacuum sintered glass funnel filter. The product was then dried at room temperature for 24 h and then at 333 K for another 24 h.

The polycarbonates produced by interfacial polycondensation with DMSO as the catalyst are obtained readily. The reaction proceeds at low temperature, so there is no need to control the process. Likewise there is no need to dry the starting materials. The process is insensitive to many impurities and environmentally friendly.

3. Results and Discussion

The general polymerization procedure described below was used to prepare various quantities of monomer(s) and different monomer combinations. (Reaction time was 120 min at 293–298 K and stirring at 2000 rpm). The different used combinations are shown in Table 1 (Fig. 2).

Different amounts of DMSO as the catalyst were also studied as well as the volume of CH_2Cl_2 used as the solvent. The synthesis was planned by using “Statgraphics Plus” program and is presented in Table 2. Measurements of viscosity were performed in these solutions and are also presented in Table 2.

Table 2

Viscosity number with different amounts of DMSO as the catalyst and CH_2Cl_2 as the solvent

Lp	DMSO		Organic phase		Viscosity number 100 cm ³ /g
	mol %	moles	cm ³	vol %	
11	240	0.016	1.1	130	0.5591
12	80	0.008	0.55	100	0.4765
13	160	0.016	1.1	160	0.4691
14	240	0.024	1.65	160	0.4417
15	240	0.024	1.65	100	0.3735
16	160	0.016	1.1	130	0.4635
17	80	0.008	0.55	130	0.7453
18	160	0.016	1.1	100	0.5158
19	80	0.008	0.55	160	0.7874
20	40	0.002	0.14	130	0.5781
21	40	0.002	0.14	100	0.5650
22	120	0.006	0.41	130	0.7545
23	120	0.006	0.41	100	0.7007

3.1. Mechanism

This synthesis is called “hetero-functional” when at least two monomers react and each monomer has at least two reactive groups [19, 20].

Polycarbonates are synthesized from BPA or BPC and bischloroformate BPA or BPC. In the reaction, one or two monomers containing two $-COCl$ functional groups and one or two bisphenol monomers containing $-OH$ groups are present (Figure 2).

The reaction proceeds at the interphase where the water phase contains BPA or BPC monomers, NaOH, DMSO as the catalyst, and deionised water whereas the organic phase contains methylene chloride as the solvent and bischloroformate BPA or BPC (Fig. 3).

The first step in the synthesis of polycarbonate from BPA or BPC is treatment of monomers with sodium hydroxide. This deprotonates the hydroxyl groups of the monomer molecule. After this the hydroxyl group forms, and the monomers with $-OH$ functional group will be in the form of sodium salt of BPA or BPC, which is more

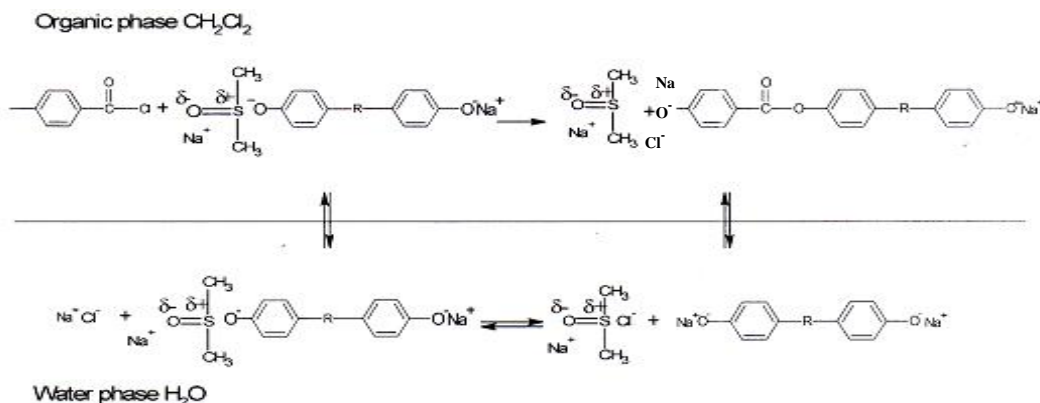


Fig. 3. Interfacial polycondensation with DMSO as the catalyst

reactive and more soluble in the water phase. Strict stoichiometry of bisphenol and sodium hydroxide is required as excess sodium hydroxide will reduce the molecular weight.

The role of the catalyst is to transfer the sodium salt of BPA or BPC from water to organic phase. It is done by separation of sodium cations and bisphenol anions in the solution. It is probable that DMSO is linked with sodium ion (Na^+) creating Na DMSO^+ cation, which is stable during the reaction and is bonded by an ion pair to the bisphenol anion as a strongly polarized molecule

containing a positive charge on the sulphur atom and molecular negative charge on the oxygen atom. The chemical behaviour and properties are based on the resonance structures shown below (Fig. 4).

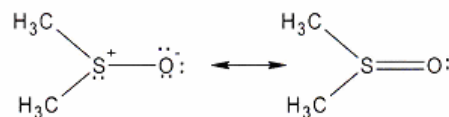


Fig. 4. DMSO resonance structures [21]

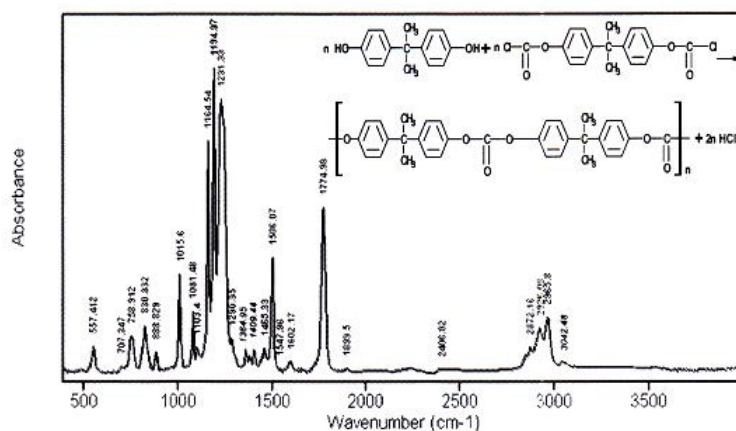


Fig. 5. BPA + Bischloroformate BPA monomers

Table 3

Group absorption frequencies

Frequency, cm^{-1}	The groups of absorption frequencies
3042–2872	C–H stretching vibrations
1780–1770	C=O stretching vibration
1607–1509	C=O carbonylic compound (sharp band)
1225–1090	Aromatic ring 1:4 substituted (weak intensity) C–O esters of aromatic acids C–O phenol stretching vibrations
1103–1015	addition to phenol group
~970	C=CCl ₂ halogeno-organic compound stretching vibrations (Figs. 7-8)
850–750	C(CH ₃) ₂ skeletal vibrations (doublet) (Figs. 5-9)
1360–1410	C(CH ₃) ₂ deformation vibrations (doublet) (Figs. 5-9)
765–755	C=CCl ₂ organo-halogen compound stretching vibrations (Figs. 7-8)

In the organic phase the transferred monomers react with bischloroformate BPA or BPC dissolved in methylene chloride. When the reaction is complete DMSO links in the organic phase with an ion pair (Na^+Cl^-) and, as the complex is transferred to the aqueous phase, decreases the unwanted products (Cl^-) in the organic phase. The catalyst in the aqueous phase is regenerated and then bonded with the next bisphenol ion pair, enabling the next reaction event.

Following this, the salt groups on the growing molecule can react with further monomers, and in this way, the molecule grows to produce the required polycarbonate.

Precise prediction of the mechanism is difficult due to great number of different agents and the dynamics of the process. It is accepted that this process most likely proceeds according to a nucleophilic mechanism $\text{S}_{\text{N}}2$. The catalyst DMSO has a significant effect not only on the mechanism of the reaction but also on yield and molecular weight of the final PC product.

3.2. Monitoring

FTIR was used to determine the products. Spectra present PC product obtained from the different monomers (Figs. 5-8) and general group absorption frequencies (Table 3).

4. Conclusions

The polycarbonates produced by the method of polycondensation with DMSO as the catalyst are easy to obtain. The reaction proceeds at low temperature, so there is no need to control the process, and also there is no need to dry the starting materials.

Polycondensation with DMSO as the catalyst is quite fast and convenient method. DMSO is a substance of moderate toxicity. The process is insensitive to many impurities and environmentally friendly since it is fully withdrawn from the obtained polymers. However, DMSO and the organic volume in the method have a significant effect on the yield and molecular weight of the final PC

product and viscosity number. It is essential to select a suitable volume of reagents for the chemical reaction. It was observed that proper separation of the aqueous and organic phase varies with the quantities of the used monomers. The optimum combination of the organic phase and the catalyst was determined by using "Statgraphics Plus" (Table 2). It was proved that optimum volume of the organic phase is between 100-160 mol % to the water phase (Fig. 9). There is no sufficient separation of the organic phase from the aqueous layer when the lower volume is used. Following this, the DMSO optimum is between 80–120 mol % to the quantities of the used monomers. If the DMSO volume is outside this range it leads to decrease in ion-pair numbers or to decay of the water-organic phase [22].

The results presented in Table 2 show decreasing viscosity number when DMSO and the solvent is outside the optimum range (Fig. 9). The viscosity measurements indicate that final PC product is similar in properties to the PC product obtained from triethylamine as the catalyst and is suitable for injection moulding.

Continuation of the work on finding a better solvent (or mixture) and process conditions as well as on improvement of the separation process has progressed to the point where a direct route of obtaining PC from bisphenols using quaternary ammonium salts or triethylamine as the catalyst may soon challenge the indirect route through dimethyl sulfoxide as the catalyst.

Fourier-Transform Infrared (FTIR) spectroscopy was a very useful tool to monitor transient changes of particular structural units with respect to the molecular orientation phenomena occurring in polycarbonates.

Acknowledgements

The authors express their thanks to Prof. Michal Fedorynski (Warsaw University of Technology, Faculty Chemistry) for providing the real mechanism of the above presented polycondensation and for the complex of expert advices, which significantly improved the publication.

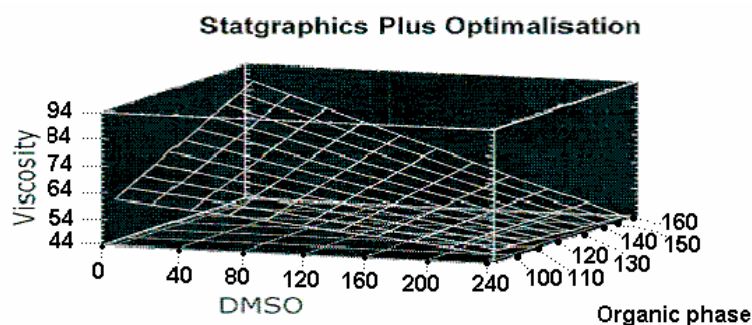


Fig. 9. DMSO and CH_2Cl_2 optimization

References

- [1] Morgan P.: Interfacial synthesis-recent advances – comments on the status and future of interfacial polycondensation. M. Dekker, New York 1982.
- [2] Porejko S., Brzozowski Z. K., Maczynski S. and Wielgosz Z.: *Chim. Ind.*, 1964, **92**, 243.
- [3] Factor A. and Orlando C.: *J Polym. Sci. Chem*, 1980, **18**, 579.
- [4] Porejko S. and Wielgosz Z.: *Polimery*, 1968, **13**, 495.
- [5] Brzozowski Z., Dubczynski J. and Petrus J.: *J. Macromol. Sci. Chem. A*, 1979, **13**, 887.
- [6] Dobkowski Z.: *Eur. Polym. Sci.*, 1982, **28**, 3105.
- [7] Dobkowski Z. and Sobkowski A.: *Appl. Polym. Sci.*, 1984, **29**, 2683.
- [8] Brzozowski Z., Dubczynski J. and Pietrus J.: *J. Macromol. Sci. Chem.*, 1979, **A13**, 875.
- [9] Brzozowski Z., Przybysz Z. and Grabowska-Rostek A.: *J. Macromol. Sci. Chem.*, 1981, **A16**, 1207.
- [10] Brzozowski Z., Jozwik B., Wojnar K. and Pruffer P.: *IUPAC Macro – 83*, Bucharest, 1983, **VII**, 347.
- [11] Noniewicz K. and Brzozowski Z.: *React. Funct. Polym.*, 1997, **33**, 343.
- [12] Brzozowski Z.: Polymer – chloral derivatives the most effective fire-safe materials, *Visnyk Nationalnogo Universitetu “Lvivska Polytechnica”*, Lwiv, Ukraine, 2000, **388**, 92.
- [13] Brzozowski Z.: *Przemysl Chemiczny*, 2003, **82**, 893.
- [14] Brzozowski Z., Staszczak S. *et al.*: *Polimery*, 2007, **1**, 29.
- [15] Zatorski W., Brzozowski Z. and Kolbrecki A.: *Polymer Degradation and Stability*, 2008.
- [16] Brzozowski Z.: ScD-habilitation, Warsaw University of Technology, 1986.
- [17] Porejko S., Brzozowski Z., Maczynski S. and Wielgosz Z.: *Chim. Ind.*, 1964, **92**, 243.
- [18] Brzozowski Z., Kielkiewicz. J. *et al.*: Polish patent 86481, 1974.
- [19] Zhang W., Westmoreland P. *et al.*: *Polymer*, 2002, **43**, 5463.
- [20] Zhang W., Westmoreland P. *et al.*: *Polymer Preprints*, 2002, **43**.
- [21] Martin D. and Hauthal H.: Dimethyl sulfoxide. Akademie-Verlag, Berlin 1971.
- [22] Brzozowski Z., Stec A. and Wielgosz Z.: Polish patent application P 363.845, 2003, Patent office decision 2008.

НОВИЙ НАПРЯМОК ДЛЯ ПОЛІКАРБОНАТІВ

Анотація. Розроблено новий напрямок одержання хімічно чистих і екологічно безпечних полікарбонатів. Показано, що процес протікає у відсутності амінів, з використанням міжфазного каталізатора диметилосульфоксиду (ДМС). Встановлено, що концентрація ДМС знаходиться в межах 80–120 % мол. в розрахунку на кількість використаних мономерів. Як бісфенольні мономери застосовано бісфенол А і бісфенол С [2,2-біс(р-гідроксифеніл)-1,1-дихлороетилен]

Ключові слова: полікарбонати, диметилосульфоксид, міжфазний каталізатор, бісфенол А, бісфенол С.