High Molar Mass Polycarbonate via Dynamic Solution Transcarbonation Using Bis(methyl salicyl) Carbonate, an Activated Carbonate

Citation for published version (APA):
Aerts, A., Kroonen, C., Kamps, J. H., Sijbesma, R. P., & Heuts, J. P. A. (2021). High Molar Mass Polycarbonate via Dynamic Solution Transcarbonation Using Bis(methyl salicyl) Carbonate, an Activated Carbonate. Macromolecular Chemistry and Physics, 222(18), [2100186]. https://doi.org/10.1002/macp.202100186

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DOI:
10.1002/macp.202100186

Document status and date:
Published: 01/09/2021

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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High Molar Mass Polycarbonate via Dynamic Solution Transcarbonation Using Bis(methyl salicyl) Carbonate, an Activated Carbonate

Annelore Aerts, Camiel Kroonen, Jan Henk Kamps, Rint P. Sijbesma, and Johan P. A. Heuts*

1. Introduction

Aromatic polycarbonates are an important class of engineering plastics that find uses in a wide range of applications due to the combination of a high toughness, optical clarity, and heat distortion resistance.\(^{[1]}\) The conventional, phosgene-free, route for bisphenol-A (BPA) polycarbonate is a high temperature melt polymerization using diphenyl carbonate (DPC) as the carbonate donor. The required high temperatures, however, make it difficult to incorporate thermally labile or volatile monomers via the conventional melt process. Using an activated carbonate such as bis(methyl salicyl) carbonate (BMSC) instead of DPC has proven to ameliorate this situation in melt polymerization allowing for significantly lower temperatures.\(^{[2–4]}\) Recently, we reported the efficient synthesis of BPA-based copolycarbonates in solution at relatively low temperatures using BMSC as the carbonate donor.\(^{[5]}\) We demonstrated the incorporation of thermally labile monomers and showed the feasibility of producing multiblock copolycarbonates via this route. In that study, however, we did not focus on any kinetic aspects and, except for one polymerization at 60 °C, all the reported polymerizations were carried out at 120 °C. In the current work, the emphasis lies on the kinetic and thermodynamic aspects of the solution polymerization of BPA and BMSC and we show that this polymerization is an almost ideal equilibrium polymerization and that very high molar masses are obtained at low temperatures without the need for removing the methyl salicylate condensate (Scheme 1).

2. Results and Discussion

First, kinetic experiments were carried out at 120, 90, and 60 °C in ortho-dichlorobenzene (o-DCB) in a closed system (details in Table 2A–C): no condensate was removed during the reaction. During these polymerization reactions, samples were taken at regular time intervals and molar mass distributions were determined via size exclusion chromatography (SEC). The absolute weight-average molar masses, \(M_w\), estimated via the Mark–Houwink parameters (see the Experimental Section) are plotted in Figure 1.

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A. Aerts
Dutch Polymer Institute
P. O. Box 902, Eindhoven, AX 5600, The Netherlands
A. Aerts, C. Kroonen, R. P. Sijbesma, J. P. A. Heuts
Supramolecular Polymer Chemistry Group and Institute for Complex Molecular Systems
Eindhoven University of Technology
P. O. Box 513, Eindhoven, MB 5600, The Netherlands
E-mail: j.p.a.heuts@tue.nl
C. Kroonen
Department of Chemistry
University of Basel
St. Johannis-Ring 19, Basel 4056, Switzerland
J. H. Kamps
SABIC
Plasticslaan 1, Bergen op Zoom PX 4612, The Netherlands

ID The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202100186

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DOI: 10.1002/macp.202100186

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202100186

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DOI: 10.1002/macp.202100186
It is clear from the data in Figure 1 that the polymerization rate increases with increasing temperature, but that the maximum achievable $M_w$ decreases.

The significantly faster rate at 120 °C as compared to 60 °C is expected and explains the difference in molar masses obtained at these two temperatures after 1 h of reaction as reported in our previous publication.[5] Assuming a negligible contribution from the reverse reaction on the initial rates and any chain length dependence of the kinetics, the bimolecular rate coefficients, $k$, for the forward reaction in Scheme 1 and as defined in Equation (1), were estimated from the data shown in Figure 1

$$\ln \left\{ \frac{(1 - rp)}{1 - p} \right\} = k \left( [\phi]_0 - [OH]_0 \right) t \tag{4}$$

The conversions, $p$, in Equation (4), are obtained from the number-average degree of polymerization, $x_n$, via Equation (5), which is obtained from a rearrangement of the general Carothers equation

$$p = \frac{(r + 1)(x_n - 1)}{2rx_n} \tag{5}$$

Analyses of the data using Equation (4) (see Supporting Information for details) yields the following estimates for $k$: $k \approx 3, 30$, and $80 \text{ L mol}^{-1} \text{ s}^{-1}$ at 60, 90, and 120 °C, respectively. Hence, the reaction rate at 120 °C is about 20–30 times faster than at 60 °C. A note should be made here that an exact determination for $x_n$ is difficult because of the inherent experimental uncertainties in determining the low $M$ side of the molar mass distribution by SEC (see Supporting Information for details).[6] Therefore, we estimated $x_n$ as $M_n/127$ and as $M_w/254$ (assuming a theoretical dispersity, $D$, of 2 and ignoring the masses of the end-groups); the differences in the obtained values for $k$ using these two approaches were small.

The second important observation in Figure 1 is that a temperature-dependent maximum $M_w$ is obtained. This observation is not surprising when considering that methyl salicylate, the condensate, is not removed from the reaction and the (net) reaction is expected to stop when equilibrium is reached. Again, assuming chain length-independent kinetics, the obtained data now enable us to estimate the equilibrium constants, $K_{eq}$, for this polymerization via Equation (6) and the results are summarized in Table 1

$$K_{eq} = \frac{p^2}{(1 - p)(r^{-1} - p)} \tag{6}$$

The obtained values of the equilibrium constants are much larger than what is commonly reported for polyesters ($K_{eq} \approx 1$) and polyamides ($K_{eq} \approx 10^2–10^3$).[7] These high equilibrium constants are explained by the fact that the methyl salicylate condensation product is stabilized by a strong intramolecular hydrogen bond.[3] Furthermore, the equilibrium constant decreases with increasing temperature, which is in line with reports in the literature for other systems.[8–11] The temperature dependence of $K_{eq}$ is most clearly seen in a so-called Van’t Hoff plot, which is shown in Figure 2 and allows for the estimation of the standard enthalpy
In order to confirm that indeed the polymerization equilibrium was obtained and to establish whether the system is truly reversible, a series of experiments was carried out in which the temperature was varied in a cyclic fashion (experiments D–F in Table 2). When equilibrium was achieved, a sample was taken and quenched in cold tetrahydrofuran (THF) before determination of the molar mass distribution by SEC. At 120 °C, the system was left to react for 2 h to make sure that the equilibrium weight-average molar mass (M\text{w,eq}) was reached after which the reaction mixture was slowly cooled to 60 °C and left overnight. This was resulted in an increase in M\text{w,eq} from 11 \times 10^3 \text{ g mol}^{-1} at 120 °C to 16 \times 10^3 \text{ g mol}^{-1} at 60 °C. This experiment was performed in three cycles in a closed system and without removal of methyl salicylate. Results of the experiments are summarized in Figure 3A, clearly showing the reversibility of the equilibrium polymerization process. The molar mass distributions for the experiment in which the temperature was cyclically varied between 120 and 60°C are shown in Figure 3B. The molar mass distributions are the same for every cycle at 120 °C, whereas the distributions of the polymers at 60 °C slightly vary. These small differences are attributed to the lower solubility of the high molar mass polycarbonate in o-DCB at 60 °C.

The same experiment was also performed between 120 °C and room temperature (Figure 3A, exp F) and also here a variation at low temperatures was observed because of the low solubility of the polymer. When the temperature was increased to 160 °C, a decrease in molar mass was observed, but now (because of the good solubility) the same molar mass was reproduced in every cycle (Figure 3A, exp E). For details on the latter two experiments, the reader is referred to the Supporting Information.

Although the equilibrium molar masses obtained in these experiments are already close to typical molar masses of commercial polycarbonates (M\text{w,eq} \approx 17 \times 10^3 \text{ g mol}^{-1} for optical quality Lexan resin\textsuperscript{[16]})\textsuperscript{,} we tried to push the molar mass to higher values by removing the methyl salicylate before carrying out a second polymerization step in solution. Starting from a polycarbonate synthesized at 60 °C (M\text{w,eq} \approx 16 \times 10^3 \text{ g mol}^{-1}), we removed the methyl salicylate by precipitation in hexane (1:15 v/v) and continued the polymerization at 120 °C (because of the lower polymer solubility at 60 °C). In this step, M\text{w,eq} increased to 46 \times 10^3 \text{ g mol}^{-1} and after repeating this step once more, the obtained M\text{w,eq} of 67 \times 10^3 \text{ g mol}^{-1} (Figure 3C) was very close to the theoretical maximum of 70 \times 10^3 \text{ g mol}^{-1} (calculated from the Carothers equation for p = 1 and r = 0.9929). This clearly illustrates the favorable equilibrium conditions for this system even at 120 °C. It is interesting to note here that the obtained M\text{w,eq} is about twice as high as the M\text{w,eq} of typical commercial sheet-grade polycarbonates.\textsuperscript{[13]}

From the results above, it is clear that equilibrium polymerization at lower temperatures would be desirable for obtaining higher molar masses, but is limited by the poorer polymer
Figure 3. A) Overview of the obtained molar masses (in $10^3$ g mol$^{-1}$) for the reversibility experiments (exps. D–F, Table 2). B) Equilibrium molar mass distributions obtained in the temperature cycling experiments between 60 and 120 °C with $[\text{BMSC}]_0 = 0.30$ m (exp D, Table 2). C) Molar mass distributions of polycarbonate synthesized in an equilibrium polymerization at 60 °C before removal of methyl salicylate ($M_w \approx 16 \times 10^3$ g mol$^{-1}$, dotted line) and after removal of methyl salicylate and subsequent equilibrium polymerizations at 120 °C: once ($M_w \approx 46 \times 10^3$ g mol$^{-1}$, dashed line) and twice ($M_w \approx 67 \times 10^3$ g mol$^{-1}$, solid line).

Figure 4. Molar mass distributions for polycarbonate synthesized with $[\text{BMSC}]_0 = 0.76$, 0.30, and 0.07 m (Table 2, I, D, and G) at 120 °C.

solubility. Therefore, polymerizations were conducted at 120 °C using lower starting concentrations of BMSC (i.e., $[\text{BMSC}]_0 = 0.76$, 0.30, and 0.07 m) while the ratios of monomers and catalysts were kept the same. The obtained molar mass distributions are shown in Figure 4. As can be seen from this figure, lowering the concentration results in a significant change of the molar mass distribution at lower $M$. Since at lower concentrations the chance of a reactive end group finding another chain or monomer decreases, the probability for cyclics formation increases and this seems clearly to be the case here.

The experiments related to Figure 4 (i.e., exps. I, D, and G in Table 2, respectively) were conducted in a cyclic fashion between 120 and 60 °C, similar to what was done in experiment D (Figure 3A); the results shown in Figure 4 correspond to the first heating at 120 °C. However, in contrast to the case of experiment D, the reactions at lower concentrations are less reversible, as the maximum attainable $M_w$ at 60 °C decreases in every cycle (see Figure S6, Supporting Information). This is also consistent with the presence of cyclics, which are not able to participate further in chain extensions.

3. Conclusions

In this work, it was shown that the solution polymerization of BMSC and BPA is characterized by a very high equilibrium constant, allowing for the synthesis of high molar mass polycarbonate without the need for removal of the condensate. Kinetic and equilibrium studies show that the system can be adequately described by the general Carothers’ equation in combination with the determined equilibrium constants. Without removal of the condensate, the system was shown to be completely reversible when changing the temperature. Only at very low starting monomer concentrations, the formation of cyclics led
to deviations from the predicted behavior. Overall, the current study further emphasizes the great potential for building in thermosensitive monomers at low temperatures and the potential for recycling and modification through the dynamic character of the system.

4. Experimental Section

4.0.0.1. General: BMSC (SABIC, 99+ %), BPA (SABIC, polymerization grade, > 99%) were kindly provided by SABIC. All other chemicals used were purchased from Sigma Aldrich, Merck, Cambridge Isotopes Laboratories, or Biosolve and used as received unless stated otherwise. 1,2-Dichlorobenzene was dried over molecular sieves (4 Å) prior to use. SEC was performed in THF at 25 °C on a Shimadzu Prominance-LC-2030C 3D equipped with a RID-20A detector and calibrated by narrow polystyrene standards. The following Mark–Houwink–Sakura parameters were used to convert the polystyrene (PS) masses into polycarbonate (PC) masses: $K_{PS} = 1.41 \times 10^{-4}$ dL g$^{-1}$, $\alpha_{PS} = 0.70$, $K_{PC} = 4.12 \times 10^{-4}$ dL g$^{-1}$, $\alpha_{PC} = 0.69$.[12]

4.0.0.2. General Polymerization Approach: Details for all polymerizations are shown in Table 1. In most experiments, $\approx 2$ g BPA, $\approx 3$ g BMSC, and $\approx 1$ mg NaOH were added to a flame-dried three neck round bottom flask, equipped with a septum, reflux cooler, tap, and stirring bar. This solid mixture was flushed with argon before the addition of $\approx 10-40$ mL o-DCCB to the flask. The resulting reaction mixture was heated to the desired reaction temperature, under constant stirring and argon flow. When the reaction was finished, the reaction mixture was poured into a 15-fold excess of $n$-hexane to precipitate the polymer. The resulting white polymer was collected by filtration and dried in a vacuum oven at 40 °C overnight.

4.0.0.3. Kinetic Experiments: First, a reaction mixture of BPA and BMSC in o-DCCB was prepared. The resulting mixture was heated to the desired temperature and stirred under argon flow. NaOH was added via a 0.2 μL syringe filter. The reaction mixture with an argon-flushed needle and syringe. The preparation of SEC samples was performed by quenching $\approx 0.1$ mL of the reaction mixture in 0.5 mL cold THF. After evaporation of the solvent using a rotary evaporator, the obtained polymer was dissolved in 1.5 mL THF and filtered through a 0.2 μm PTFE syringe filter.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge SABIC for supplying polymerization grade BPA and BMSC. The Dutch Polymer Institute is gratefully acknowledged for funding; this work forms part of the research program of DPI, project #80515.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon request.

Keywords

kinetics, polycarbonate, solution polymerization, thermodynamics, transcarbonylation

Received: May 25, 2021
Revised: July 8, 2021
Published online: August 2, 2021

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