POLYCARBONATE DIOLS TO PRODUCE ELASTIC POLYURETHANE FOAMS – A METHOD OF IMMOBILIZATION OF CARBON DIOXIDE INTO A POLYMER STRUCTURE

Kiril Dimitrov1, Dimitrina Todorova2, Sanchi Nenkova2, Michael Herzog1

1 University of Applied Sciences Wildau
Hochschulring 1, 15745 Wildau
Germany
E-mail: dimitrov@th-wildau.de
2 University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria

Received 04 July 2016
Accepted 07 October 2016

ABSTRACT

Using carbon dioxide as feedstock for polymers is a big challenge and a chance for our sustainable future. It has an immense potential for the coming decade, which comes much faster than expected. Scientists are very active lately in carbon dioxide chemistry research, especially in the field of carbon dioxide based chemicals and polymers.

We report here on the stability of higher molecular weight polycarbonate diols and the formation of specialty polyurethanes such as UV stable elastomers, semi-rigid foams, and elastic sealants. These polyurethanes are produced from polycarbonate diols (ETERNACOLL®) and aromatic 4,4’-diphenyl-methane diisocyanate, from aliphatic hexane-1,6-diamocyanate, or the trimer, diisocyanates. We use butane-1,4-diol or pentane-1,5-diol as a chain extender. The thermal and mechanical properties of the polyurethanes obtained are determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The data obtained show no phase segregation or any type of crystallinity. Any possible changes in the molecular mass distribution of the samples are investigated with the application of gel permeation chromatography (GPC). It is evidenced that only heat treatment brings about molecular mass distribution shifts to lower values.

Keywords: polycarbonate polyols, synthesis, polyurethanes, foams.

INTRODUCTION

One of the major issues of present-day polymer chemistry is the substitution of fossil carbon by renewable sources. These may be biologically based carbon materials [1 - 3] or materials obtained through incorporation of carbon dioxide (CO2) into the polymer chain by formation of carbonate units [4]. The latter may be found in polycarbonates as homopolymers or in polycarbonate based building blocks, e. g. as polycarbonate polyols produced on the ground of alkylene oxides and CO2 [6], by the coupling reaction of an epoxide such as 1,2-epoxy-4-cyclohexene with CO2 in the presence of a ZnCl2/nBu4NI catalyst system [9], by polycondensation of carbonates [10], or from monomer diols and carbonates [5]. The polycarbonate diols are used to produce elastomers by typical urethane formation via diisocyanates or by a condensation reaction along a non-isocyanate route [11].

The classical route to produce polyurethane elastomers using polycarbonate diols, methylene-bis 4-phenylisocyanate (MDI) and butane-1,4-diol is used. The properties investigated show an increase of the hard-segment content as a result of the formation of larger hard domains of a higher crystallinity. Thus higher mechanical properties such as higher tensile stress, tear strength, and hardness compared to those of the conventional polyether based types are obtained [12]. The study of polyurethane elastomers formation based on polycarbonate diols shows that these substances provide the formation of a multitude bubbles, which is indicated by some gas cleavage during production. This observation leads to considering ways of polyurethane products stabilization either by development of suitable polymer structures or by different additives introduction. Another feature of these polyols is their high viscosity, which
is usually in the range of 100 Pas. The decrease of the mixtures viscosity during the formulation of the systems is essential for meeting the processing conditions. In the present study, new polycarbonate polyols are investigated and used for the synthesis of polyurethanes. Finally, new ways to obtain stable and workable formulations of elastomers, sealants, and semi-rigid foams are found out.

**EXPERIMENTAL**

**Materials and Methods**

Polycarbonate diols with the brand name ETERNACOLL® were obtained from UBE Europe S. A., Castellon, Spain. Their nominal molecular masses were equal to 2000 Da. The properties are listed in Table 1.

The chain extenders butane-1,4-diol, hexane-1,6-diol and dipropylene glycol were obtained from Elastogran AG, while pentane-1,5-diol was purchased from UBE Europe S. A. All chain extenders were used after degassing (100°C/1 Torr). Solid MDI, a liquefied MDI by pre-polymerization with triethylene glycol (Lupranat® MP 105) and a liquefied MDI (mixture of isomers) (Lupranat® MIP) were obtained from Elastogran AG. The solid MDI was used as a melt at 46°C (stored at 46°C to 47°C, only the clear supernatant was used). The trimerized aliphatic hexane-1,6-diisocyanate (HDI) was received from Performance Chemicals HGmbH as a symmetrical trimer (PC ISO 23®) and an asymmetrical trimer (PC ISO 24®). They were used as received.

Potassium oleate as a 20 % solution in dipropylene glycol was used as a catalyst. It was received as PC CAT® TKO. N,N,N’,N’-tetramethyl guanidine was received as PC CAT® TMG. Stannous neodecanoate was received as PC CAT® T 7, di-n-octyl-tin dicarboxylate was provided as PC CAT® T 130, dibutyl tin dilaurate was obtained as PC CAT® T 12, while dibutyl tin-bis(2-ethylhexylthioglycolate) was purchased as PC CAT® T 16. All these reactants were products of Performance Chemicals HGmbH. The foam stabilizer DC 193 was provided by Dow Chemical Corp.

**Synthesis**

Elastomers were produced after degassing the ETERNACOLL® at 130°C/1 torr for three hours. After this, the water content was lower than 0.02 %. The ETERNACOLL® was mixed with the chain extender and the catalyst(s) by stirring (500 rpm, 15 min) and degassed again (room temperature, 0.1 torr). The mixture was heated to 70°C. The calculated amount of the respective isocyanate was added to this mixture. The latter was thoroughly mixed for 10 min at 70°C, degassed for 1 min at 0.1 torr and poured into aluminium pans. Curing was performed for one hour at room temperature or at 80°C.

Foams were produced on the ground of ETERNACOLL® as received by adding the calculated amounts of chain extender and catalysts to form a pre-mix. The calculated amount of isocyanate was added to it. The start time, the rise time, and the tack free times were noted during the foaming process. The density and hardness were determined after 24 hours at room temperature.

**Characterization techniques**

The hydroxyl numbers, the acid numbers, and the isocyanate content were chemically determined by titration in accordance with the standards accepted. The hydroxyl numbers were determined using acetic anhydride with the application of the pyridine method. The acid numbers were obtained on the ground of the alcoholic potassium alcoholate method, while the isocyanate content was found by proceeding a reaction with di-n-butylamine in toluene and back-titration of the excess by hydrochloric acid against bromo-phenol blue.

Density measurements were carried out using a cube of 5 cm side length. Its weight was measured on an analytical balance (Sartorius AG, SECURA 224-1CEU) and hence the density was simply calculated.

The shore hardness was determined using a Zwick Shore durometer for Shore A, Shore 0, and Shore 00 ranges.

The mechanical properties were identified using a Zwick Universal investigate machine Z20.

The DSC curves were recorded by a Netzsch DSC 204 Phoenix under nitrogen in the range between -150°C and +250°C at a rate of 10 K min⁻¹. This procedure was followed by cooling to -150°C and a subsequent running of the measurement (two or three measurements were carried out).

GPC was performed using a Varian 920-LC equipped with a Shodex GPC KF-803 column and a RI detector. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min⁻¹. The columns and the detectors were thermostated at 30°C. The GPC calibration curves were constructed using selected polyether polyols.

DMA was performed using an automatic Myrenne
pendulum ATR3 at 1 Hz under nitrogen and a heating rate of about 1 K min\(^{-1}\) in the range from -175°C to +150°C.

**RESULTS AND DISCUSSION**

**Investigation of the stability of ETERNACOLL\(^{®}\) 1 and 2**

A mass loss is observed during the 1st run of DSC study of poly(carbonate-urethane) elastomers in the temperature region between 30°C to 90°C. But this effect is absent during the second run (see Fig. 1 for an example).

The mass loss could not be attributed to the polymer structure as it is typically observed in case of gas losses. Hence it is assumed that the polymer lost some of its carbon dioxide content either within the macromolecular chains or through absorption by the carbonate groups of the polycarbonate diol. The glass transition from -19°C to -7°C is another indicator of chain scission in the material on heat treatment. It suggests that the main phase consists of shorter structural units.

Possible changes in the molecular mass distribution of the samples are investigated using GPC to learn more about the origin of the mass loss.

The data from GPC show that the molecular mass distribution shifts to lower values only as a result of heat treatment - the original sample has a maximum at ca. 4000 Da with a rather narrow distribution, while that obtained upon heat treatment is shifted to about 1800 Da with a much broader distribution (see Fig. 2). This suggests a partial chain cleavage and loss of CO\(_2\) in its course. It is also indicative of polycarbonate diol sensitivity to temperatures at least above 100°C.

The decomposition starts nearly immediately in the presence of a catalyst after heating to 70°C (see Fig. 3). The process of degradation continues with time as seen in the GPC curve after 15 hours treatment. The formation of low molecular mass products compared to the original reactants is well outlined. This fact supports the analysis and the interpretation that low molecular mass splitting products result from low and high temperature treatment.

When investigating the stability of the polycarbonate diols at higher temperature the effect of degradation is much stronger. The experiment carried out for 7.5 hours at 255°C shows a decrease in the maximum in the polycarbonate diol curve from ca. 3600 Da down to

![Fig. 1. DSC curves of ETERNACOLL\(^{®}\) 1 – pentane-1,5-diol – Lupranat\(^{®}\) MP 105 Polyurethane.](image)

<p>| Table 1. Properties of ETERNACOLL(^{®}) types as received. |
|-----------------|-----------|-----------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Type/item</th>
<th>Mn (GPC)</th>
<th>OH No. [mg KOH/g]</th>
<th>Acid No. [mg KOH/g]</th>
<th>Viscosity 25°C [mPas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2017</td>
<td>55.6</td>
<td>&lt; 0.1</td>
<td>277 900</td>
</tr>
<tr>
<td>2</td>
<td>1839</td>
<td>61.0</td>
<td>&lt; 0.1</td>
<td>56 060</td>
</tr>
</tbody>
</table>
about 1000 Da (see Fig. 4). After 24 hours the maximum reaches a value of ca. 400 Da. This is clear evidence for the splitting of the polycarbonate chains (see Fig. 5) and the formation of mainly short chains.

The results of these investigations show that the polycarbonate chains are sensitive to heat. These experiments are repeated with both ETERNACOLL® types in presence of the catalysts PC CAT® TKO and PC CAT® TMG. The addition of small amounts of these compounds (0.1 % b. w.) to both ETERNACOLL® types results in decrease of the polycarbonate diols within a short period of time. The values obtained range from 50 % to 10 % of the original one suggesting a chain scission in presence of strongly alkaline substances.

The data obtained in case of ETERNACOLL® 1 and 2 % of PC CAT® TKO are listed in Table 2.

It is evident that the thermal treatment as well as the addition of alkaline substances leads to a dramatic reduction of viscosity and to an increase of the hydroxyl number. This is a clear indication of chain scission and molecular mass loss, which in turn suggests instability of the carbonate chains formed.

**Formation of poly(carbonate urethane) elastomers**

The elastomers studied are produced from an aromatic diisocyanate, Lupranat® MP 105 based on MDI. The reactant is liquefied in the course of a reaction with a small amount of tripropylene glycol. In general, elastomers on this basis, which are independent of the

Table 2. Changes in properties of ETERNACOLL® 1 during thermal treatment and in the presence of a catalyst.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>OH-No. KOH/g [mg]</th>
<th>Viscosity 25°C [mPas]</th>
<th>Viscosity 75°C [mPas]</th>
<th>Weight loss [%]</th>
<th>Weight loss gas [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>55.6</td>
<td>277 900</td>
<td>2 550</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15 h/70°C</td>
<td>206.0</td>
<td>53 900</td>
<td>693</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>Distillation at 255°C</td>
<td>280.0</td>
<td>9 430</td>
<td>248</td>
<td>33.4</td>
<td>32.0</td>
</tr>
<tr>
<td>2 % PC CAT® TKO (15h/70°C)</td>
<td>97.0</td>
<td>53 900</td>
<td>693</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig 3. GPC protocol of ETERNACOLL 1 of the original sample (A), the sample with added catalyst PC CAT® TKO (B), the sample treated at 70°C for 8 hours in the presence of the catalyst (C), and after 15 hours in the presence of PC CAT® TKO at 70°C (D).

Fig 4. GPC protocol of ETERNACOLL 1 of the original sample (A) and after distillation at 255°C for 7.5 hours (B).
chain extender and catalyst used, tend to foam or form more or less bubbles. Even after degassing the reaction mixture discolors during the curing process and shows a mass loss in the temperature range of 30°C to 100°C in the course of DSC study. One example is presented in Fig. 1, while another one using butane-1,4-diol as a chain extender is shown in Fig. 6.

The DSC curve shows that a massive mass loss occurs in the range between 25°C and 140°C, while a very slight mass loss occurs during the second run. It is also insignificant during the third run but at temperatures lower than 200°C, i.e. below the range of polyurethanes typical decomposition. The glass transition increases from -1°C within the first run to +5°C during the subsequent runs without a recognizable difference. This is an indication that the cleavage has already occurred at rather low temperatures and is completed at 150°C. Besides this takes place within the short time of the measurement, two hours roughly in this case.

Several experiments carried out in presence of ETERNACOLL® 1 catalyst with formulations modified by the chain extenders used give very similar results. This motivates the choice to use this polycarbonate diol to produce semi-rigid foams (see the following paragraph).

The experiments aimed to produce poly(carbonate-urethane) elastomers from ETERNACOLL® 2 were somewhat more positive but showed a slight mass loss during the first run of the DSC measurements (see Fig. 7). It can be seen that the difference between the first and second run is much less than that observed in the course of poly(carbonate urethane) elastomer formation using ETERNACOLL® 1. Another positive change is that the glass transition temperature does not change after the first run and remains constant at -10°C. This suggests that ETERNACOLL® 2 based on hexane-1,6-diol and pentane-1,5-diol is much more stable than ETERNACOLL® 1. This is further supported by the experiments of degassing and distillation under nitrogen. The mass loss measured during treatment for three hours at 110°C and 4 mbar is 2.9 % only. This is less than the 10 % mass loss observed in case of ETERNACOLL® 1. This confirms the findings in ref.[5] referring to the effect of the polycarbonate diols structure on the properties of the elastomers formed.

In the search of possible solutions to decrease thermal instability effect hexane-1,6-diisocyanate trimers are used as an isocyanate component. The change for HDI trimer is outlined in case of ETERNACOLL® 1 but the effect is not as pronounced as that in case of ETERNACOLL® 2. Fig. 8 depicts the DSC curve of
the formulation of ETERNACOLL® 1, butane-1,4-diol and PC ISO® 24 which is to be compared to the DSC curve shown in Fig.6.

An endothermic peak signalling a loss of material (gas) is seen in the range from 25°C to 100°C. The glass transition temperature shifts from -21°C to -8°C. The chain scission is not clearly hindered by changing the isocyanate in case of ETERNACOLL® 1. In case of using ETERNACOLL® 2 and hexan-1,6-diisocyanate trimer the endothermic peak signalling a loss of gaseous substances is much smaller and shifted to higher temperatures (see Fig. 9). The glass transition is shifted from -12°C during the first run to -8°C during the second one suggesting slight modifications of the polycarbonate chain.

Another way to influence the elastomers thermal behaviour refers to a change of the chain extender. Butane-1,4-diol and pentane-1,5-diol are used in the elastomers discussed so far. They tend to form segregated structures with MDI containing hard and soft
domains. In fact the hard domains may crystallize or form ordered structures. The DSC curves show that there are no peaks showing any segmented or crystalline structure (no melting exothermic or crystallization endothermic peaks). The formation of ordered or segmented structures in polyurethane elastomers is strongly hindered by using dipropylene glycol as a chain extender. Therefore, dipropylene glycol, instead of butane-1,4-diol or pentane-1,5-diol, is used as a chain extender in the formulations discussed so far.

The DSC curve of a formulation based on ETERNACOLL® 1, dipropylene glycol and Lupranat® MP105 is shown in Fig. 10. The glass transition is only slightly affected, while the endothermic peak at 74°C is somewhat smaller but clearly seen. A continuous degradation of the material starting from about 85°C is observed during the second run. It shows that the thermal stability of the material has not really increased and remains as fragile as in case of the material made with butane-1,4-diol.

This experiment is repeated with ETERNACOLL® 2. The DSC curve obtained is depicted in Fig. 11. It shows a small endothermic peak at 85°C recorded during the
first run. The comparison with the peak obtained with the same material but in presence of ETERNACOLL 1 shows it is much smaller and shifted to higher temperature values. This suggests a higher thermal stability of this elastomer compared to that shown in Fig. 10.

The DSC curve depicted in Fig. 12 refers to ETERNACOLL® 1, dipropylene glycol, and PC ISO® 24 formulation. It shows the essential difference with respect to stability of the formulations made either with butane-1,4-diol or pentane-1,5-diol or mixtures thereof. A first glass transition is observed at -19°C during the first run and at -16°C in the course of the second one. This indicates little post-curing of the material. A second glass transition is found at +22°C and +28°C during the two runs, correspondingly. It is attributed to the phase of the dipropylene glycol and the aliphatic isocyanate. Except this second glass transition, there is no evidence of a decomposition or loss of carbon dioxide in the temperature range up to 120°C. The results just presented verify the stabilizing effect of dipropylene glycol in this formulation. None of the investigated systems show any indication of crystallization of the polycarbonate diols or the polyurethanes prepared from them. This contrasts the suggestion in ref. [17] referring to the DSC curves.
endothermic peaks. It explains their appearance as a result of crystalline phase melting without ever taking into consideration the decomposition of the polycarbonate diols in presence of traces of the corresponding alkaline calcium catalyst.

The results presented here point to the fact that alkaline substances have to be thoroughly avoided in polycarbonate based polymer systems. Otherwise, a loss of the material stability has to be expected. A stabilizing effect is achieved by the proper choice of the reactive additive. We find that dipropylene glycol shows the best stabilizing effect in the polyurethane systems using both MDI and T-HDI. No deterioration of the mechanical or light stability properties is observed.

The poly(carbonate urethane) elastomer formed on the ground of ETERNACOLL® 2, dipropylene glycol, and PC ISO® 24 as depicted in Fig. 13 is a relatively thermally stable material in a broad temperature range as shown by the DSC curve of Fig. 13.

There is still a small endothermic peak at 80°C. But the glass transition is shifted only by 2°C during the second run, while no change occurs during the third run after exposition to a temperature of 200°C. The Shore A hardness of the material is 40 in contrast to that of the material made from Lupranat® MP105 whose value is 55. The Shore hardness does not change within 30 days.

The structure elucidation is performed by DMA. An example referring to an elastomer produced of 1 mol ETERNACOLL® 2, 1 mol butane-1,4-diol, and 2 mol of PC ISO® 24 is shown in Fig. 14. The data presented shows a distinct glass transition region at a relatively low temperature despite of using a trifunctional isocyanate. The low temperature transitions at -130°C or -90°C reflect the starting mobility of the side chains. There is no indication of phase segregation or crystallinity present in the material.

The poly(carbonate urethane) elastomers produced on the ground of ETERNACOLL® 2 and PC ISO® 24 have molar ratios ranging from 1 : 1 to 1 : 4 (polycarbonate : diol). Butane-1,4-diol, pentane-1,5-diol, or dipropylene glycol are used as a chain extender to obtain clear, colourless elastomers. The molar ratio variation brings about Shore A hardness of values between 10 and 80. Such elastomers cannot be obtained from the same formulations but in presence of poly(ethylene carbonate) diol possibly because of the higher hydrophilic nature of the ethylene oxide units [14].

Semi-rigid foams

The observation of reactive systems foaming in case of production of elastomers from ETERNACOLL® 1 provides the assumption that the formation of foams could result in high quality products by stabilizing the cells during the foaming process. Both sources of CO₂, i.e. CO₂ absorbed by the carbonate groups and CO₂ resulting from cleavage processes can be used in studying the reaction mixture foaming. Thus, only ETERNACOLL® 1 is used in the first experiments to produce foams with a
density in the range from 650 g/dm³ to 130 g/dm³. Some examples are presented in Table 3.

It is seen that semi-rigid poly(carbonate-urethane) foams can be prepared in a broad range of density and hardness. No auxiliary foaming agent is required to obtain the foams described. Table 3 shows that the hardness strongly depends on the chain extender and not so much on its molar ratio in respect to ETERNACOLL® 1 or isocyanate. In case of dipropylene glycol as the chain extender, the effect of the catalyst is shown to exceed any other effect. A low density at a reasonable hardness can be achieved only by using PC CAT® TKO. The less alkaline TMG gives only about half the foam volume, while the typical tin catalyst (PC CAT® T9)

Fig. 13. Poly(carbonate urethane) elastomer formed of ETERNACOLL® 2, dipropylene glycol, and PC ISO® 24 in the presence of PC CAT® T7 and PC CAT® T16.

Fig. 14. DMA of the poly(carbonate urethane) elastomer produced of 1 mol ETERNACOLL® 2, 1 mol butane-1,4-diol, and 2 mol of PC ISO® 24 (storage modulus $G'$, loss factor $\tan \delta$, complex loss modulus $G''$).
has the least effectiveness and provides more or less a cellular elastomer but no real foam. It is found that when ETERNACOLL® 2 is used, the foaming can be achieved only by the addition of water as an auxiliary foaming agent. These experiments are not reported here.

**CONCLUSIONS**

The experiments reported above show that polycarbonate diols are a valuable tool to produce different types of poly (carbonate-urethanes). The formulation of such products requires taking into account the fact that the composition of the diols of the carbonate chain has a marked effect on the thermal stability both of the polycarbonate diols and the resultant elastomers or semi-rigid foams. In case of ETERNACOLL® 1 the stability is much lower than that in case of ETERNACOLL® 2 based on pentane-1,5-diol and hexane-1,6-diol. This behaviour affects the quality of the foams. The use of ETERNACOLL® 1 envisages the careful adjustment of the catalyst amount and the reaction time to exclude core discolouration in the foams. It is also shown that the strongly alkaline catalyst PC CAT® TKO is an active catalyst in respect to the reaction of the polycarbonate diols and the isocyanates used. It is worth noting that such highly alkaline substances lead to further thermal instability of the resultant polyurethanes. This instability is higher when aromatic isocyanates are used when compared to that found in presence of aliphatic isocyanates. Furthermore, the chosen chain extender is of importance. We observe that the change from straight hydrocarbon chains of C2 to C6 to ether – dipropylene glycol leads to an increase of the thermal stability which may result from the higher flexibility of the ether oxygen.

The thermal treatment of the elastomers based on ETERNACOLL® 1 as it is done during the DSC analysis brings about thermal instability of this product at rather low temperatures. An endothermic peak is seen in all samples based on the aromatic diisocyanate MDI in the temperature range from 30°C to 100°C. This effect is found in presence of any chain extender investigated. The peak pointed above is attributed to gas evolution. There are two possible reasons in this case: CO₂ absorption by the carbonate chain (which may contribute to the peak at the lower temperatures) and CO₂ evolution because of chain scission. The amount of CO₂ obtained is such in some cases that semi-rigid foams are produced from ETERNACOLL® 1 in absence of any auxiliary blowing agents.

The investigation of the elastomers by DSC and DMA reveals no phase segregation or any type of crystallinity. No verification is found even in case of using butane-1,4-diol and MDI known to form segregated phases. The use of a trimerized aliphatic isocyanate leads in case of ETERNACOLL® 2 to the formation of highly elastic, transparent, and UV stable elastomers in a hardness Shore A range from 20 to 80. These elastomers, especially those having Shore A hardness of 45 to 55, are extremely useful as sealant materials in closures or in an electrical equipment. DSC measurements and investigations in a climate chamber at 80°C shows properties stability within at least 30 days. This suggests a stabilizing effect of the asymmetrically trimerized HDI (PC ISO® 24) (lminoxadizindione trisocyanate) on poly(carbonate urethanes). Furthermore, the chain extenders investigated have also some effect on the stability of the poly(carbonate urethanes). Butane-1,4-diol leads to the highest defects in course of thermal treatment. They are slightly lower when pentane-1,5-diol is used and in fact the lowest when dipropylene glycol, usually not considered at all, is used as a chain extender.

The poly(carbonate-urethanes) based on ETERNACOLL® 2 and PC ISO® 24 show a typical thermoplastic behaviour in spite of the crosslinked nature of the

Table 3. Density and Shore A hardness of semi-rigid foams produced of ETERNACOLL® 1 (stabilizer used in all cases DC 193).

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Chain extender</th>
<th>Molar ratio</th>
<th>Density [g/dm³]</th>
<th>Shore A hardness</th>
<th>catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP 105</td>
<td>Butane-1,4-diol</td>
<td>1 : 3 : 4</td>
<td>271</td>
<td>30</td>
<td>TKO</td>
</tr>
<tr>
<td>MP 105</td>
<td>Butane-1,4-diol</td>
<td>1 : 4 : 5</td>
<td>452</td>
<td>35</td>
<td>TMG</td>
</tr>
<tr>
<td>Lupranat®</td>
<td>Butane-1,4-diol</td>
<td>1 : 3 : 4</td>
<td>147</td>
<td>33</td>
<td>TKO</td>
</tr>
<tr>
<td>MP 105</td>
<td>dipropylene glycol</td>
<td>1 : 5 : 6</td>
<td>228</td>
<td>70</td>
<td>TKO</td>
</tr>
<tr>
<td>MP 105</td>
<td>dipropylene glycol</td>
<td>1 : 5 : 6</td>
<td>494</td>
<td>90</td>
<td>TMG</td>
</tr>
<tr>
<td>MP 105</td>
<td>Butane-1,4-diol</td>
<td>1 : 4 : 5</td>
<td>648</td>
<td>80</td>
<td>T9</td>
</tr>
</tbody>
</table>
material. Their thermal decomposition occurs at a much higher temperature, usually above 200°C as shown by DSC. This corresponds to the generally higher thermal stability of the aliphatic substituted polyurethanes [15].

Semi-rigid foams of a broad density and hardness can be obtained using the polycarbonate diols, especially ETERNACOLL® 1, in absence of any additional blowing agents [16]. This is unexpected and suggests the absorption of some CO$_2$ by the polycarbonate chains.

The use of polycarbonate diols based on various starter diols provides the adjustment of the properties of the resultant elastomers or semi-rigid foams. Different chain extenders, di- or triisocyanates, or catalysts can be added. Extremely low reaction times and low densities of the semi-rigid foams are achieved by using unusual highly alkaline catalysts such as the potassium olate (PC CAT® TKO).

**Acknowledgements**

The authors acknowledge the support of Mr. Kornejew of TH Wildau for GPC performing, to Mrs. Knoll of TH Wildau for DSC measurements, and to Mrs. Werner of TH Wildau for assistance in preparation of the elastomer and foam samples.

**REFERENCES**

6. Z. Zhou, Z. Cao, Y. Liang, Y. Zhang, J. Lin, R. Chich (Bayer Materials Science), Polyurethane Microcellular elastomer, method for preparing same and use thereof, WO 2010/115567 (14. 10. 2010); Bayer: Schaumstoff für Matratzen aus CO$_2$, plastericker 01. 08. 2013