

Process for the recycling of polycarbonates

5 The present application relates to a process for the chemical-material recycling of low-molecular polycarbonate residues, production waste, remainders, recyclates and similar polycarbonate compositions by condensation to produce technically utilisable higher molar masses, polycarbonates from this recycling process, their use, and moulded bodies and extrudates from these polycarbonates.

10 Polycarbonates, for example from bisphenol A, are mostly amorphous technical thermoplastics with high-quality properties, such as e.g. high transparency, thermoforming resistance and toughness. The same applies also to aromatic copolycarbonates that are built up, for example, from bisphenol A and a cobisphenol. The production costs of such materials and the level of their properties
15 thus also justify more demanding recycling processes, if old moulded parts or production scrap are to be sent for ecologically-necessary and economically-reasonable recycling. The divide between processing costs and economy is considerably more beneficial for aromatic polycarbonates than for many other thermoplastics, so that processes consisting of more than one process step are
20 fundamentally also worthwhile. However, efforts are always being made to find processes that are simpler and more economic than the known processes, in order to be able to produce more cheaply.

25 As with other thermoplastics, the level of mechanical and physical properties of polycarbonate depends decisively on the molecular weight. However, production waste, recyclates etc. frequently do not, or no longer, possess the required molecular weights. Direct material recycling of production waste or recyclates is therefore possible only to a very limited extent.

30 When recycling polycarbonate residues, production wastes, remainders, recyclates and similar polycarbonate compositions, it is therefore desirable and essential to

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increase the molecular weight to a level sufficient for the projected new use. So, it is desirable, for example, to increase low-molecular production scrap from PC production for Compact Discs to the molecular weight range required for injection moulding. Or the average molecular weight of PC recyclate from the de-lamination of Compact Discs is to be increased sufficiently to allow the material to be used e.g. as a component in the production of PC/ABS blends.

There is little reference in the literature to condensation of polycarbonate moulding compositions destined for chemical-material recycling. Thus EP-A 931 810 discloses a process for increasing the molecular weight of decomposed low-molecular polycondensates such as polyamides, polyesters and polycarbonates using reactive chain lengtheners. These chain lengtheners react in the plastic melt, e.g. in an extruder, under conventional compounding conditions, with the functional chain ends of the polymer. Special bisepoxides are mentioned as chain lengtheners, alone or in combination with, inter alia, epoxides, bisoxazolines, dicyanates, tetracarboxylic acid dianhydrides, bismaleic imides and carbodiimides. However no example is given for the functioning of the process with polycarbonate. The applicant's own trials showed no increase in the molecular weight of polycarbonate using the process described in EP-A 931 810.

DE-PS 43 26 906 provides a process for the chemical recycling of polycarbonate by transesterification with hydroxy compounds, in particular phenol, until bisphenol and the esterified carbonate unit are obtained, followed by resynthesis of polycarbonate in the melt. Although in this process bisphenol and the carbonate unit are obtained, the polycarbonate is first completely decomposed by transesterification. In addition to the decomposition of useful bonds, which must then be built up again, the process method is also complex and expensive.

DE-OS 42 40 314 differs from the above patent specification substantially by prior decomposition of the polycarbonate to oligomers, by transesterification with low-boiling monophenols. Then a higher-viscosity oligomer with a particular content of

OH terminal groups is produced first from the decomposition product and optionally added diarylcarbonate by recondensation with the splitting off of the monophenol, which, in the final stage, is then polycondensed in the melt under more rigorous reaction conditions to form the desired polycarbonate. Here too the polycarbonate is first decomposed, which necessitates an additional process step. A further disadvantage is that oligomers with OH terminal groups are significantly more susceptible to thermal and oxidative loading than the corresponding polymers and rapidly become discoloured and damaged. The condensation process is therefore sensitive and must be subjected to complex controls to achieve a precise reaction that minimises such effects.

Finally, DE-OS 44 21 701 discloses a process for the chemical recycling of polycarbonates by decomposition with diaryl carbonates to form oligomers. After they have been crystallised in a particular solvent, cleaned and dried, these are recondensed to form polycarbonate, optionally with the addition of bisphenols and a catalyst. The disadvantages of this recycling process are the same as those of the processes according to DE-PS 43 26 906 and DE-OS 42 40 314, described above.

On the basis of this prior art, the object was therefore to provide a process by which the molecular weight of polycarbonates can be increased as simply and efficiently as possible.

It was found that, surprisingly, it is possible to condense polycarbonates by simple melting in a vacuum, optionally with bisphenols or suitable oligocarbonates with OH terminal groups, to produce, directly, polycarbonates of higher molecular weights.

The present invention thus relates to processes for the condensation of polycarbonate, characterised in that polycarbonates can be condensed in the melt, usefully with the addition of bisphenols or oligocarbonates with OH terminal groups

to accelerate the reaction, optionally using catalysts, wherein polycarbonates are obtained, which have a higher molecular weight than the starting polycarbonate.

5 In the process according to the invention, the polycarbonate to be condensed, preferably bisphenol A-polycarbonate, as a granulate or ground PC moulded parts, is transferred to the melt using suitable machines, and then condensed in a reactor device operating batch-wise or continuously. Suitable values for the reaction parameters for this are pressure, temperature and residence time. If necessary, suitable catalysts should also be chosen and added.

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Suitable reaction parameter ranges are for example 0.01 to 5 mbar, preferably 0.1 to 2 mbar, 250-350°C melting temperature, preferably 280-320°C and average residence times of 0.01 to 0.3 hours for screw-type or extruder machines and 0.2 to 4 hours for agitated tanks, kneading apparatus and disk or basket reactors. When using
15 disk or basket reactors, residence times of 0.5 to 2 hours are preferred.

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With discontinuous processes, pressure and temperature can be varied in a time programme up to and within the given ranges. Continuous processes are normally run constantly under the suitable temperature and pressure conditions, wherein pressure and temperature profiles can be set along the length of the reactor.

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Embodiments preferred, preferred in particular or most particularly preferred are those in which the parameters, definitions and explanations stated under preferred, preferred in particular or most particularly preferred, are used.

However, the general definitions, parameters or explanations, or those listed in preferred ranges, given above and below can also be combined arbitrarily with each other, i.e. between the particular ranges and preferred ranges.

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The polycarbonate used either already has an average concentration of phenolic terminal groups of over 100 ppm OH, preferably 100 – 1500 ppm, in particular 400

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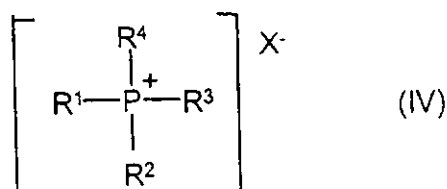
– 1000 ppm, or this is specifically set in the melt by the addition of bisphenols, preferably bisphenol A, or oligocarbonates with OH terminal groups. When converting in the melt to higher molecular weights, volatile portions that are split off are discharged from the reactor device via the vapours. The small quantities arising here are sluiced out of the process by suitable means, which simplifies the process considerably.

Condensation can be carried out in suitable agitated tanks, screw- or kneading apparatus, extruders, disk or basket reactors and in combinations of such apparatus. For continuous processes, extruders or basket or disk reactors, in particular basket or disk reactors are preferred, as disclosed in DE Appl. No. 1 011 98 51 or DE –C2 44 47 422. Basket or disk reactors are also suitable for discontinuous processing.

Condensation must be accelerated optionally by the addition of a condensation catalyst. Suitable catalysts and the concentrations in which to use them can be taken from the literature (Chemistry and Physics of Polycarbonates, Polymer Reviews, H. Schnell, Vol. 9, Pages 44-51, John Wiley & Sons, 1964; DE-PS 1 031 512; EP-A 360 578; EP-A 351 168; US-A 3 442 854).

Alkali- or earth alkali compounds with an alkaline action and ammonium- or phosphonium salts, hereinafter described as onium salts, are preferred.

Phosphonium salts according to the invention are those of the formula (IV),



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wherein R^{1-4} can be the same or different C_1 - C_{10} -alkyls, C_6 - C_{10} -aryls, C_7 - C_{10} -aralkyls or C_5 - C_6 -cycloalkyls, preferably methyl or C_6 - C_{14} -aryls, in particular

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methyl or phenyl, and X^- can be an anion such as hydroxide, sulfate, hydrogen sulfate, hydrogen carbonate, carbonate, a halogenide, preferably chloride, or an alcoholate of the formula OR, wherein R can be C_6-C_{14} -aryl or C_7-C_{12} -aralkyl, preferably phenyl.

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Preferred catalysts are

tetraphenylphosphonium chloride

tetraphenylphosphonium hydroxide

tetraphenylphosphonium phenolate

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in particular tetraphenylphosphonium phenolate.

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Further preferred catalysts, which can be used alone or optionally in addition to an onium salt, are compounds of alkali metals and earth alkali metals with an alkaline action, such as hydroxides, alkoxides and aryloxides of lithium, sodium, potassium, magnesium and calcium, preferably of sodium. Sodium hydroxide and sodium phenolate and the sodium bisphenolate of bisphenol A are most preferred.

20

The polycarbonate is introduced into the condensing reactor preferably via a screw as the melting unit. If bisphenols or oligomers with OH terminal groups are added to increase the concentration of OH terminal groups, the screw is a mixing unit at the same time. A melting screen with or without a backwashing device can be positioned between the screw and the condensing reactor, to retain particular contaminant particles $\geq 5 \mu m$ from the highly fluid melt. The melt flowing from the condensing reactor after polycondensation is discharged by means of a gear pump.

Here the melt can be fed over static mixers or extruders and mixed with additives to set special formulations of the polycarbonates produced before being fed on for granulation.

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Possible additives are disclosed e.g. in WO 99/55772, pg. 15 – 25, DE Appl. No. 10122496.6 and in "Plastics Additives", R. Gächter and H. Müller, Hanser

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Publishers 1983. In principle, additives can be added at any point in the reaction, preferably before granulation.

Any bisphenol or an oligocarbonate with OH terminal groups can optionally be added to the polycarbonate to be condensed. The bisphenol or the OH-containing oligocarbonate on which the polycarbonate to be condensed is based, are preferred.

The dosage of the bisphenol or the oligocarbonate in relation to the weight of polycarbonate used is in the range 0:100 to 10:100, preferably 0.1:100 to 5:100, in particular 0.2:100 to 1:100 for the bisphenol and in the range 0:100 to 50:100, preferably 0.5:100 to 30:100, in particular 1:100 to 10:100 for the oligocarbonate.

Examples of bisphenols that can be used according to the invention or can also form the basis of the polycarbonate to be condensed can be found in WO-A1 01/05866, pg. 6-8. 4,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenyl sulfide, 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 2,2-bis-(4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α' -bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(p-hydroxyphenyl)-3,3,5-trimethylcyclohexane are preferred. Diphenols preferred in particular are 4,4'-dihydroxybiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A) and 1,1-bis-(p-hydroxyphenyl)-3,3,5-trimethylcyclohexane. 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A) and 1,1-bis-(p-hydroxyphenyl)-3,3,5-trimethylcyclohexane are preferred most particularly, in particular 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A). Accordingly the oligomers obtained from these bisphenols can also be used according to the invention.

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5 The polycarbonate used has an average molecular weight M_w of 15.000 to 30.000, preferably 16.000 to 25.000, in particular 17.000 to 22.000, determined by measuring the relative solution viscosity in dichloromethane, calibrated by light scattering. A PC recyclate is preferred, in particular a PC recyclate from Compact Discs.

10 The polycarbonates and copolycarbonates used can originate from the known phase boundary- or melt transesterification process and can therefore contain different chain stoppers.

Phenol, octylphenol, cumylphenol and t-butylphenol are suitable chain stoppers. Other typical chain stoppers for polycarbonate can be taken from WO-A1 01/05866, pg. 4-6. There can also be mixtures of chain stoppers, e.g. via the mixing of different polycarbonates. Polycarbonates from the melt transesterification process preferably
15 have the phenol of the diphenylcarbonate used for production as a chain stopper.

Both uniformly synthesised polycarbonate and a mixture of various polycarbonates can be condensed. The polycarbonates may differ with regard to their average molecular weight, the bisphenol used and/or the chain stopper used, branching agent
20 etc., used. Furthermore, the polycarbonates may contain chain branching agents. Conventional chain branching agents can also be taken from WO-A1 01/05866 pg. 8-9. Polycarbonates, which are built up of the same bisphenol, in particular bisphenol A, are preferred.

25 Mixtures occur in particular when the PC recyclates from consumption waste and process scrap to be condensed are not of the same type.

The polycarbonates obtainable by the process according to the invention can be processed on conventional machinery, for example extruders or injection moulding
30 machines, to produce any type of moulded body, for example films or sheets, in the conventional manner. Furthermore, the polycarbonates according to the invention

can also be mixed into other polymers, e.g. polyolefins, polyurethanes, polyesters, ABS and polystyrene. These materials are added preferably on conventional machines to the finished polycarbonate, but can also be added at another stage in the production process as required.

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The invention also provides the polycarbonates obtainable by the process according to the invention themselves. They differ from primary material, in other words the known commercial material, by the presence of fluorescence-active centres, which fluoresce when irradiated with UV light, e.g. black light. This optical effect can be used e.g. to aid plastic recognition in sorting processes for material recycling or to differentiate between a recyclate and a primary material.

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Auxiliary substances and reinforcing agents can be mixed into the polycarbonates according to the invention to change or improve certain properties. Thermo- and UV stabilisers, flowing agents, mould release agents, flame-retardants, hydrolysis stabilisers, finely comminuted minerals, fibres, e.g. alkyl- and arylphosphites, -phosphates, -phosphanes, low-molecular carboxylic acid esters, halogen compounds, salts, chalk, quartz meal, glass and carbon fibres, pigments, dyes and combinations thereof, amongst others, can inter alia be considered for this purpose. Such compounds are disclosed e.g. in WO 99/55772, pg. 15-25 and in "Plastics Additives", R. Gächter and H. Müller, Hanser Publishers 1983.

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These additives can be dosed e.g. into the melting and discharge screw or directly into the melting reactor, although the discharge unit is preferred.

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The polycarbonates produced according to the invention can be used for many mechanically demanding applications. They are thus suitable for the production of moulded bodies and extrudates of the most varied character. Possible applications are

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- Safety screens, which, as is known, are needed in many areas of buildings, vehicles and aircraft, and as visors for crash helmets,
- Films, in particular ski films,
- Blown bodies (see for example US Patent 2 964 794), for example 1 to 5
5 gallon water bottles,
- translucent sheets, in particular multi wall sheets, for example for covering buildings such as train stations, greenhouses and lighting installations,
- optical data storage units,
- traffic signal housings or traffic signs,
- 10 - foamed materials (see for example DE-AS 1 031 507),
- threads and wires (see for example DE-AS 1 137 167 and DE-OS 1 785 137),
- translucent plastics with a glass fibre content for lighting purposes (see for example DE-OS 1 554 020),
- 15 - translucent plastics containing barium sulfate, titanium dioxide and/or zirconium dioxide or organic polymeric acrylate rubbers (EP-A 634 445, EP-A 269324) for the production of translucent and light-diffusing moulded parts,
- small, precision injection-moulded parts, such as for example lens mounts
20 (polycarbonates containing glass fibres, which optionally also contain ca 1 – 10 wt.% MoS₂, in relation to the total weight, are used for this),
- optical instrument parts, in particular lenses for cameras and camcorders (see for example DE-OS 2 701 173),
- light transmission media, in particular fibre-optic cables (see for example
25 EP-A1 0 089 801),
- electrical insulation materials for electrical conductors and for plug housings and pin-and-socket connectors,
- mobile telephone housings with improved resistance to perfume, after-shave and perspiration,
- 30 - network interface devices,
- carrier materials for organic photoconductors,

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- lights, e.g. headlamps, light-diffusing screens or internal lenses,
- medical applications e.g. oxygenators, dialysers,
- food applications, such as e.g. bottles, cutlery and chocolate moulds,
- applications in the automotive industry, where there may be contact with
- 5 fuels and lubricants, such as e.g. bumpers, optionally in the form of suitable blends with ABS or suitable rubbers,
- sports equipment such as e.g. slalom poles or ski boot buckles,
- household articles such as e.g. kitchen sinks and letter box housings,
- housings, such as e.g. electrical distributor cases, housings for electric
- 10 toothbrushes and hairdryer housings,
- transparent washing machines – portholes with better resistance to washing solution,
- protective goggles, vision-correcting spectacles,
- lamp covers for kitchen fittings with improved resistance to kitchen vapours,
- 15 in particular oil vapours,
- packaging films for medicines,
- chip boxes and chip carriers,
- as well as other applications such as e.g. stable doors or animal cages.

20 The following examples are intended to illustrate the object of the present application without restricting it.

Example 1

Ground PC from the de-lamination of Compact Discs by the process described in
5 EP-A 537 567 (pg. 1, 2, 5, 6) was melted, after pre-drying in the circulating air dryer
(2 h/120°C) in a twin shaft screw ZSK 25 (Werner & Pfleiderer), and continuously
fed into a basket reactor at 300°C. A mixture of 0.25 wt.% bisphenol A, in relation
to the polycarbonate used, with part of the polycarbonate to be condensed was
simultaneously weighed into the melting screw. In all, the PC feed stream via the
10 feed screw was 20 kg/h. No condensation catalyst was used. The condensation
reactor was a drum with a melt inlet and outlet at the ends and a vacuum connection
in the gas space, in which a shaft with disks, which dipped into the melt, slowly
rotated. The speed of rotation was 0.8 revolutions per minute; the average residence
time of the melt was ca 180 minutes. The melt temperature was 300°C, the pressure
15 in the gas space of the reactor was 0.7 to 0.8 mbar. The condensed melt was
discharged via a gear pump with attached granulating unit. The properties of the PC
granulate thus obtained and the starting material are summarised in Table 1.

Table 1: Condensation of recyclate from Compact Discs (after de-lamination) in a disk reactor

Properties	Dimension	Start ¹⁾	Condensates ²⁾	
		A	B	C
			(A+BPA)	(A+BPA)
Mechanical				
Elongation at break	%	3.5	82	91
Impact strength				
IZOD impact strength, RT	kJ/m ²	28	n.b.	n.b.
IZOD	kJ/m ²	8 b	67t	
notched impact strength, RT		61t/17b		
Contents				
Phenolic OH	ppm	600	500	600
Flowability				
MVR 300°C/1.2 kg	cm ³ /10 min	65	16	23
rel. solution viscosity	-	1.202	1.271	1.248
1) A: CD recyclate, recovered by de-laminating ground material from CDs				
2) B: A + 0.25 wt.% BPA, 310/300°C, 0.8 mbar, 180 min average residence time				
C: A + 0.25 wt.% BPA, 300/290°C, 0.7 mbar, 180 min average residence time				
b = brittle; t = tough; n.b. = not broken				

Example 2

- 5 Similarly, low-molecular PC granulate from production waste was condensed to produce a higher-molecular polycarbonate. As before, Bisphenol A was used here but no condensation catalyst. The material values were summarised comparatively in Table 2.

Table 2: Condensation of low-molecular PC granulate for the production of Compact Discs in a disk reactor

Properties	Dimension	Start ¹⁾	Condensate ²⁾
		D	E
		Makrolon DP 1-1265	(D+BPA)
Mechanical			
Elongation at break	%	60	100
Impact strength			
IZOD impact strength,	kJ/m ²	28	n.b.
RT			
IZOD	kJ/m ²	10	60
notched impact			
strength, RT			
Contents			
OH	ppm	130	550
Flowability			
MVR 300°C/1.2 kg	cm ³ /10 min	71	40
rel. solution viscosity	-	1.195	1.223
1) D: primary material granulate			
2) E: D + 0.25 wt.% BPA, 320/310°C, 0.75 mbar, 180 min average residence time			

Example 3

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Finally, ground PC from the de-lamination of Compact Discs was also condensed in an extruder. The extruder used was a twin shaft screw ZSK 32 (Werner & Pfleiderer) 1.4 m long with a 0.8 m long de-aerating dome, beginning 0.4 m along

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the screw length. Here too, melt condensation was carried out without the addition of a transesterification catalyst. Before being added via dosing scales, the material was pre-dried in a recirculating air dryer (2 h/120°C). The results are summarised in Table 3.

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Table 3: Condensation of Compact Disc-recyclate after de-lamination on a twin shaft screw (ZSK 32, Werner & Pfleiderer)

Properties	Dimensions	Start ¹⁾	Condensate ²⁾
		F	G
		(from F)	
Mechanical			
Elongation at break	%	2.7	61
Impact strength			
IZOD impact strength, RT	kJ/m ²	11b	n.b.
IZOD			
notched impact strength, RT	kJ/m ²	35b	n.b.
Contents			
OH	ppm	440	140
Flowability			
MVR 300°C/1.2 kg	cm ³ /10 min	82	18
rel. solution viscosity	-	1.202	1.255
Condensation of another starting material (F') adding 0.25 wt.% BPA:			
OH content	ppm	260	120
rel. solution viscosity	-	1.198	1.265

1) F: CD recyclate, recovered from the de-lamination of ground material from CDs

2) G:F melt condensed at 320-340°C, 0.5-l mbar, 2 kg/h throughput, 100 rpm, 3-5 min average residence time

b = brittle; n.b. = not broken

Measuring methods:

5 Elongation at break, modulus of elasticity to ISO 527; impact/notched impact strength to ISO 180/1C or ISO 180/4A; phenolic OH photometrically with TiCl_4 on the Ti complex; MVR to ISO 1133; rel. solution viscosity on PC solution in dichloromethane (5 g PC/l).

10 It can clearly be seen that with the process according to the invention, the molecular weight of low-molecular polycarbonates (A, D, F) can be condensed to averagely- and highly-viscous polycarbonates (B, C, E, G) with better mechanical properties such as elongation at break and impact/notched impact strength.

Claims

1. Process for the condensation of aromatic polycarbonates and copolycarbonates, characterised in that the (co)polycarbonate having a weight average molecular weight of 15.000 to 30.000, is melted in suitable units and the melt is fed into a suitable reactor device operated batch-wise or continuously, optionally with the addition of a bisphenol or oligocarbonate with OH terminal groups and optionally a transesterification catalyst, and the polycarbonate melt is subjected to a melt transesterification reaction in the temperature range 250-350°C, at a pressure below 5 mbar and a residence time of 0.02 - 4 hours.
2. Process according to claim 1, characterised in that it is carried out in a temperature range of 280-320°C.
3. Process according to claim 1, characterised in that the molecular weight of the polycarbonates and copolycarbonates used is regulated with the conventional phenolic chain stoppers.
4. Process according to claim 1, characterised in that the polycarbonate or copolycarbonate is used in a mixture with a bisphenol in a weight ratio of 100:0 to 100:10 or with an oligocarbonate with OH terminal groups in a weight ratio of 100:0 to 100:50.
5. Process according to claim 1, characterised in that the condensation of the melt is accelerated with a conventional transesterification catalyst for polycarbonate.
6. Process according to claim 1, characterised in that mixtures of different polycarbonates are condensed.

7. Polycarbonate, characterised in that it is obtainable by the process according to claim 1.
8. Use of the polycarbonate according to claim 7 for the production of moulded bodies and extrudates.
9. Use of the polycarbonate according to claim 7 for the production of blends with other thermoplastics such as ABS and various polyesters.
10. Moulded bodies and extrudates of polycarbonate according to claim 7.