(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 061 079 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.12.2000 Bulletin 2000/51

(51) Int. Cl.[7]: **C07D 313/04**, C08G 63/08

(21) Application number: **99201957.0**

(22) Date of filing: **17.06.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant:
SOLVAY (Société Anonyme)
1050 Bruxelles (BE)

(72) Inventors:
- **Wautier, Henri**
  7090 Braine-Le-Comte (BE)
- **Latere, Jean-Pierre**
  4020 Liege (BE)
- **Lecomte, Philippe**
  4000 Cointe (BE)
- **Jerome, Robert**
  4845 Sart-Jalhay (BE)
- **Dubois, Philippe**
  4260 Ciplet (BE)

(74) Representative:
Eischen, Roland et al
Solvay S.A.
DCRT-IAM-PI-ID
Rue de Ransbeek 310
1120 Bruxelles (BE)

(54) Cyclic esterketone compounds and processes for the synthesis and use thereof

(57) Cyclic esterketone compounds, and in particular, 2-oxepane-1,5-dione, which are useful as a monomer for the production of polymers, and in particular for the production of poly(2-oxepane-1,5-dione). Processes are also disclosed for both the synthesis of this new compound and for the use (polymerization) thereof for the preparation of poly(2-oxepane-1,5-dione). The poly(2-oxepane-1,5-dione) polymers and copolymers which are obtained by use of the polymerization processes with the monomer compounds are also disclosed.

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Description

[0001] The present invention relates to new cyclic esterketone compounds which are useful as monomers for the production of polymers, and in particular for the production of poly(2-oxepane-1,5-dione), to processes for both the synthesis thereof and the use thereof for the preparation of polymers and to the polymers obtained therewith.

[0002] In recent years there has been a strong preoccupation with the development of biodegradable and nontoxic polymers which may be used for replacing existing polymers. To be useful for such purposes, the polymers must also possess other properties of the polymers which they are intended to replace. Such properties include, inter alia, permeability, biocompatibility, promotion of bioadhesion and reactivity for attachment to drugs.

[0003] In this regard, various aliphatic polyesters derived from lactones have drawn interest. Of particular interest in this regard are those aliphatic polyesters derived from lactones and, in particular, those derived from ε-caprolactone. Polymers derived from ε-caprolactone (such polymers being referred to herein as Pε-CL) are one of the very few commercially available biodegradable polymers, being well known for its biocompatibility, permeability and biodegradability. Pε-CL also possesses the rare property of being miscible with a variety of other polymers (such as PVC), thereby permitting them to be formed therewith into polymer blends/alloys (e.g., copolymers) in which deficient properties of the other polymer(s), such as poor stress/crack resistance, gloss and adhesion, are ameliorated.

[0004] Pε-CL has been as particularly desirable for the replacement of certain polymers, vinylic and otherwise in plastic bags and in films and wrappings. Unfortunately, due to a relatively low melting point of about 60°C, the ability for Pε-CL to be employed to replace such polymers in such uses is extremely limited, with an increase of at least 20°C being necessary.

[0005] To resolve the above-mentioned problems, a new polymer, poly(2-oxepane-1,5-dione) (also known, and referred to herein, as PKCL) has been synthesized which possesses a melting point of about 150°C and a glass transition temperature of about 41°C. This polymer, is formed from the monomer 1,4,8-trioxaspiro[4,6]-9-undecanone (also known as TOSUO) in a well-controlled "living" ring-opening polymerization reaction using aluminum isopropoxide [$Al(OiPr)_3$] as an initiator, whereby polyTOSUO is formed, followed by a reaction for 1 hour at 25°C using Ph_3CBF_4 and CH_2Cl_2, whereby PKCL is formed.

[0006] TOSUO is, in turn, synthesized according to a Baeyer-Villiger reaction by the oxidation of 1,4-cyclohexanedione monoethylene acetal by 3-chloroperoxybenzoic acid (m-CPBA) at 40°C in CH_2Cl_2.

Unfortunately, the synthesis of TOSUO follows a pathway that requires separate steps, the first wherein the functions of the ketone are shielded and the second wherein the acetal functions are deshielded, thereby complicating and increasing the cost and time required for the synthesis.

[0007] Accordingly, it can be seen that there remains a need to provide a compound which is useful as a new monomer that may be polymerized to form poly(2-oxepane-1,5-dione) (PKCL), which monomer compound may also be directly synthesized from the starting material in high yield using a one-step process. It can further be seen that there remains a need to provide a process to form PKCL from the monomer compound, as well as a need to provide the PKCL polymer so obtained,

[0008] It is a first primary object of the present invention to provide a compound which is useful as a new monomer that may be polymerized to form poly(2-oxepane-1,5-dione), so that said compound may be used to replace TOSUO for use in producing PKCL.

[0009] It is a further object of the present invention to provide such a compound which may be easily obtained from the starting material in one-step.

[0010] It is a second primary object of the present invention to provide processes whereby the cyclicesterketone compound of the present invention may be produced from starting material in one-step.

[0011] It is a third primary object of the present invention to provide PKCL polymers formed by the polymerization of the monomer compound of the present invention.

[0012] It is a fourth primary object of the present invention, to provide processes whereby the monomer compound of the present invention is polymerized for the producing PKCL.

[0013] In accordance with the teachings of the present invention, disclosed herein are novel compounds which are useful as monomers for the production of polymers, and in particular for the production of poly(2-oxepane-1,5-dione). These compounds are also simple and easy to synthesize from their starting materials in high yield using a one-step process that involves the oxidation (and, particularly, mono-oxidation) of the starting material (and particularly, cyclic diketones, such as 1,4-cyclohexanedione).

[0014] More precisely, disclosed herein are novel cyclic esterketones that are useful as monomers in the production of, e.g., PKCL. Preferably, these cyclic esterketones are chosen from appropriate oxepane-diones. Most preferred is 2-oxepane-1,5-dione (referred to herein as KCL).

[0015] KCL is a particularly attractive compound for use as a monomer due to, inter alia, its long-term stability which translates into a good shelf life. In this regard, KCL has a shelf-life, in open air at ambient temperature, of at least three months. Further, it may be conserved without substantial degradation for more than three months at -20°C, in an inert

nitrogen atmosphere. Such long-term stability is important in the measure where the KCL may be prepared in large quantities, with all the benefits that are derived from such an economy of scale.

[0016] KCL is further particularly useful due to the ease by which it may be synthesized in a one-step reaction by oxidation of the starting material.

[0017] In another aspect of the present invention, disclosed herein are processes for the synthesis of the novel cyclic esterketone compounds of the present invention, and in particular of 2-oxepane-1,5-dione (KCL), that permit the compound to be easily and simply prepared directly from the starting material in one step.

[0018] The processes of the present invention for the synthesis of KCL permit that (monomer) compound to be easily and simply prepared in one-step directly from the starting material. In other words, the (monomer) compounds of the present invention (including the cyclic esterketones and, more particularly, 2-oxepane-1,5-dione) are obtainable by these processes of the present invention.

[0019] In particular, the process of the present invention involves the oxidation (e.g., mono-oxidation) of cyclic diketones (to esters) to produce cyclic esterketone monomers. Preferably, these cyclic diketones are saturated cyclic diketones. Most preferred is 1,4-cyclohexanedione (which is used to synthesize KCL).

[0020] As will be readily understood (and as is capable of being determined) by one skilled in the art, the precise concentration of the starting material to be employed in the processes of the present invention may be varied as needed to obtain the precise quantities of the (monomer) compounds of the present invention desired.

[0021] Nonetheless, it is contemplated herein that at least 0.01 M of starting material will be employed in the processes of the present invention. Preferably, at least 0.06 M of starting material will be employed in the processes of the present invention. Also preferred is the use of at least about 0.14 M of starting material. Still further preferred is the use of at least about 0.17 M of starting material. Most preferred is the use of at least about 0.2 M of starting material. In this regard, use of concentrations of 0.33 M, 0.55 M, 0.85 M and 0.99 M of starting material in the processes of the present invention are particularly preferred.

[0022] As used herein, the symbol "M", when referring to concentrations (of, e.g., starting material, oxidant, catalysts, initiators, etc.), is used to stand for molarity (moles of the substance per liter of the solution).

[0023] Preferably, the cyclic diketones useful in the present invention are oxidized (mono-oxidized) (to esters) by an oxidant that is, preferably, a peracid. This is especially the case where 1,4-cyclohexanedione is the cyclic diketone and the compound (i.e., monomer) desired to be obtained is 2-oxepane-1,5-dione (KCL).

[0024] In this regard, it is preferred that the peracid is a perbenzoic acid or a chloroperacid. Particularly preferred in this regard is that the chloroperacid is chloroperbenzoic acid. Most preferred is that the chloroperbenzoic acid is metachloroperbenzoic acid.

[0025] The precise peracid chosen may be any which is suitable for the task as can be determined by one skilled in the art. However, it is contemplated herein that where 1,4-cyclohexanedione is used to synthesize KCL, use of a metachloroperbenzoic acid is most preferred.

[0026] It is contemplated herein that the oxidant to be used to oxidize (mono-oxidized) the starting material may be generated "in-situ". This is particularly the case when the oxidant is a peracid.

[0027] In order to generate the oxidant (e.g., peracid) "in-situ", it is contemplated herein that an aldehyde will be provided which will be reacted (in-situ) with oxygen (O_2).

[0028] An example of such an instance is addition of benzaldehyde (PhCHO) and oxygen to the starting material, in such a case, the oxygen reacts with the benzaldehyde to generate the peracid oxidant (perbenzoic acid) which then oxidizes the starting material. Another example is the addition of either a para-, ortho- or meta-chlorobenzaldehyde and oxygen to the starting material to generate, respectively, para-, ortho- or meta- chloroperbenzoic acid.

[0029] In such cases, the aldehyde is added as such and the oxygen is bubbled into the reaction medium by the use of any known apparatus which are well-known and used in the art for such a purpose.

[0030] As will be readily understood (and as is capable of being determined) by one skilled in the art, the precise concentration of the peracid or, in the event that "in-situ" generation of the peracid is desired), the aldehyde and the oxygen to be employed in the processes herein varies depending upon the precise starting material, peracid, etc., which is used.

[0031] Nonetheless, it is contemplated herein that for every mole/liter (M) of starting material employed in these processes, at least 1 mole/liter (M) of peracid will also be employed. Preferably, at least 1.1 M of peracid will be employed for every 1.0 M of starting material employed in the processes of the present invention. Further preferred is the use of at least about 2.0 M of peracid will be employed for every 1.0 M of starting material. Still further preferred is the use of at least about 3.0 M of peracid will be employed for every 1.0 M of starting material.

[0032] It is further preferred that no more than about 3.0 M of peracid for every 1.0 M of the starting material be used in the processes of the present invention.

[0033] In the process for the synthesis of the novel monomer compounds of the present invention, the precise conditions and times under which the oxidation of the starting material is performed may be optimized according to the starting material used, the monomer compound desired and/or the concentrations thereof, as may be determined by

one skilled in the art.

[0034] Nonetheless, as to time, it is contemplated herein that oxidation of the starting material will be carried out for at least about 10 minutes. It is further contemplated herein that oxidation of the starting material will be carried out for up to about 48 hours. However, it should be understood that, if desired or needed, the processes may be carried out for periods of less than 10 minutes and/or for more than 48 hours.

[0035] As to temperature, it is contemplated herein that oxidation of the starting material will be carried out at a temperature of at least about 0°C. It is further contemplated herein that oxidation of the starting material will be carried out in temperatures of up to about 120°C. However, it should be understood that, if desired or needed, the processes may be carried out in temperatures of less than 0°C and/or more than 120°C.

[0036] It is contemplated that the preferred operating conditions will be to carry out oxidation of the starting material for about 1 hour to about 24 hours at a temperature in the range of about 20°C to about 80°C. Particularly preferred is to carry out oxidation of the starting material at about 40°C.

[0037] It is further preferred that oxidation of the cyclic diketones to form the monomer compounds according to the processes of the present invention be carried out in the presence of a solvent. The solvent which is chosen for the synthesis of the monomers of the present invention may also be anyone which is suitable for the task as can be determined by one skilled in the art. Particularly preferred in this regard are dichloromethane and 1,2-dichloroethane.

[0038] Finally, it is noted that it is preferred that the oxidation of the cyclic diketones, and in particular of 1,4-cyclohexanedione, according to the processes of the present invention be done under the action of a catalyst. Examples of catalysts which would be useful in this regard are $Ni(acac)_2$, $Ni(dmp)_2$ which stands for bis-(dipivaloylmethanota)nickel (II) (ref: Yamada, T.; Takahashi, K.; Kato, K.; Takai, T.; Inoki, S.; Mukaiyama, T. *Chem. Lett.* 1991, 641), $Ni(OAc)_2$, $Cu(OAc)_2$ (ref: Bolm, C.; Schlingloff, G.; Weickhardt, K. *Tetrahedron Lett.* 1993, *34*, 3405), heteropolyoxometalates (ref: Hamamoto, M.; Nakayama, K.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem*. 1993, *58*, 6421), iron (III) oxide, cobalt(III) oxide (ref Li, X.; Wang, F.; Zhang, H.; Wang, C.; Song, G. *Synth. Commun*. 1996, *26*, 1613). In this regard, it is preferred that the catatyst be iron (III) oxide.

[0039] The precise catalyst(s) to use and the precise concentration thereof to employ in the processes of the present invention will vary depending upon various factors as will be readily understood by one skilled in the art.

[0040] In still another aspect of the present invention, disclosed herein are (polymerization) processes for the preparation of polymers, and in particular of PKCL which can be used to replace Pε-CL. These processes are characterized by the polymerization of the novel cyclic esterketone compounds of the present invention, and in particular of 2-oxepane-1,5-dione.

[0041] These processes may be either solution polymerization processes or mass polymerization processes, as desired and as can be readily decided on and determined by those skilled in the art.

[0042] Polymerization of the novel cyclic esterketone compounds of the present invention, and in particular, of 2-oxepane-1,5-dione, can be promoted by any type of initiator known in the art. Particularly attractive are metal alkoxides, the metal of which contain free p, d or f orbital of a favorable energy, e.g., Mg, Ti, Zr, Zn, Sn, Al, Y, La, Hf and rare earth atoms, such as Sm.

[0043] Preferably, aluminum isopropoxide $[Al(OiPr)_3]$ is employed as an initiator in the polymerization processes of the present invention.

[0044] As will be readily understood (and as is capable of being determined) by one skilled in the art, the precise concentration of the initiator to be employed in the processes of the present invention may be varied as needed to obtain the polymer(s) which is (are) desired to be obtained thereby. In this regard, the concentration of the initiator to employ is defined by the molecular mass which is desired to be possessed by the polymer obtained therefrom.

[0045] Polymerization of the novel cyclic esterketone compounds of the present invention, and in particular, of 2-oxepane-1,5-dione, can be promoted by any type of catalyst known in the art. Particularly attractive are metal oxides, halides or carboxylates, the metal of which contain free p, d or f orbital of a favorable energy, e.g., Mg, Ti, Zr, Zn, Sn, Al, Y, La, Hf and rare earth atoms, such as Sm, in the presence of protic species, such as alcohols, amines, thiols and water.

[0046] It is further preferred that such polymerization processes employ $Sn[OC(O)\text{-}CH(CH_2\text{-}CH_3)\text{-}(CH_2)_3\text{-}CH_3]_2$ (herein referred to as stannous octoate) as a catalyst.

[0047] As will be readily understood (and as is capable of being determined) by one skilled in the art, the precise concentration of the catalyst to be employed in the processes of the present invention may be varied as needed to obtain the polymer(s) which is (are) desired to be obtained thereby.

[0048] It is further contemplated herein that polymerization of the novel cyclic esterketone compounds of the present invention, and in particular of 2-oxepane-1,5-dione, may further be promoted by the use of any type of the aforementioned catalysts/initiators both in solution with apolar to medium polarity solvents, and in bulk (without any solvent).

[0049] The precise operating conditions and times to employ in the process for the polymerization of the novel monomer compounds of the present invention may be readily determined and optimized by one skilled in the art according to the process employed, the concentration of the starting material employed therein, the polymer desired and/or the

quantities thereof.

[0050] Nonetheless, it is contemplated herein that the polymerization of the novel cyclic esterketone compounds of the present invention, and in particular of 2-oxepane-1,5-dione, be done at a temperature which is at least 0°C. It is further contemplated herein that the polymerization of the novel cyclic esterketone compounds of the present invention be done at a temperature which is at least 20°C.

[0051] Further in this regard, it is also contemplated herein that the polymerization of the novel cyclic esterketone compounds of the present invention, and in particular of 2-oxepane-1,5-dione, be done at a temperature of up to about 180°C. It is further contemplated herein that the polymerization of the novel cyclic esterketone compounds of the present invention be done at a temperature of up to about 120°C.

[0052] However, as will be readily understood by one skilled in the art, it should be understood that, if desired or needed, the polymerization processes of the present invention may be carried out at temperatures of less than about 0°C and/or at temperatures of greater than about 180°C.

[0053] In yet another aspect of the present invention, disclosed herein is a polymer, and in particular PKCL, which is obtainable by (and which has been obtained by) the polymerization of the novel cyclic esterketone (monomer) compounds of the present invention, and in particular of 2-oxepane-1,5-dione, preferably by using the polymerization processes of the present invention.

[0054] The PKCL produced from the KCL monomers of the present invention is a particularly useful polymer for replacing, in particular, PVC in films, wrapping and garbage bags. In this regard, it is noted that this PKCL has a melting point of about 156°C and a glass transition temperature of about 41°C. Accordingly, this PKCL may be used in wide variety of applications in which Pε-CL, due to it's low melting point (about 60°C) cannot.

[0055] If desired, the KCL polymers (PKCL) of the present invention may be formed as a copolymer (including but not limited to terpolymers) by either polymerization with at least one other monomer or by mixing (with or without chemical reactivity therebetween) of polymers which have been synthesized individually (e.g. by mixing in the presence of a transesterification catalyst, such as dibutyl tin oxide). Preferably, the at least one other monomer includes ε-CL. Other types of monomers/polymers which may be combined with KCL (either with random or sequential comonomer distribution) include but are not limited to lactides, glycolides, β-, γ-, δ- and ε-lactones, substituted or not and their polymers.

[0056] In this regard, copolymers of KCL and ε-CL are particularly contemplated as being preferred.

[0057] Preferably, such P(KCL-ε-CL) copolymers have at least about 1% (w/w) KCL. More preferred is that such P(KCL-ε-CL) copolymers have at least about 5% (w/w) KCL. Most preferred in this regard is that such P(KCL-ε-CL) copolymers have at least about 8% (w/w) KCL.

[0058] Further preferred is that such P(KCL-ε-CL) copolymers have no more than about 99% (w/w) KCL. More preferred is that such P(KCL-ε-CL) copolymers have no more than about 80% (w/w) KCL. Most preferred in this regard is that such P(KCL-ε-CL) copolymers have no more than about 50% (w/w) KCL.

[0059] The P(KCL-ε-CL) random copolymers provided for by the processes of the present invention have both a high melting point (ranging from about 80°C to about 150°C) and a low glass transition temperature (ranging from about -20°C to about 35°C).

[0060] Unless specifically otherwise stated, as used herein, the terms "polymer" and "polymer resin" are used to refer to and include homopolymers, copolymers, terpolymers, etc., and blends and alloys thereof.

[0061] Unless specifically otherwise stated, as used herein, the term "copolymer" refers to those polymers which are formed from two different monomers and includes block, graft, random and alternating polymers and blends and alloys thereof In this regard, the polymer which comprised the copolymer may be either formed together, such as when at least two different types of monomers are polymerized at the same time and in the same reactor (commonly referred to as copolymerization) or they may be formed separately and mixed together either with or without reactivity therebetween.

[0062] Having thus described the novel cyclic esterketone (monomer) compounds of the present invention, the processes for the synthesis thereof, the PKCL polymers produced therewith and the processes for the polymerization thereof, the following examples are now presented for illustrative purposes only and are not meant to limit the scope of the invention.

Example 1

Synthesis of KCL monomer compound

[0063] A sample of KCL monomer was prepared as follows.

[0064] Into a two-neck glass reactor equipped with a septum and a three-way stop cock and a cooling jacket on which is mounted a gas-exhaust valve the following was added:
0.17 M of 1,4-cyclohexanedione (98% by weight) (ALDRICH), 0.5 M of benzaldehyde (99 % by weight, distilled before use) (ALDRICH), 0.001667 M of Fe_2O_3 (99.999 % by weight, 100 mesh) (ACROS) and 60 ml of 1,2-dichloroethane (J.T.

BAKER 8042) (assay (GC) minimum 99.5% w/w) which had been dried over molecular sieves (4 Å) (ALDRICH) just before use.

[0065] The reactor was then placed under magnetic agitation in an oil bath at 40°C for 6 hours with oxygen bubbled into the reaction medium through a capillary tube, so as to saturate the solution.

[0066] After the six hour period, the oxygen bubbling was ceased and the temperature in the reactor was permitted to drop to 20°C before opening.

[0067] After evaporation of the solvent under reduced pressure, using a rotary film evaporatory (BUCHI water bath B-480), the precipitate was recovered.

[0068] The recovered crude product was then analyzed and the conversion to 2-oxepane-1,5-dione was determined by ^{1}H-NMR.

[0069] ^{1}H-NMR spectra of the 2-oxepane-1,5-dione (KCL) obtained was recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN400 superconducting magnetic system at 25°C.

[0070] The results of this analysis revealed that the precipitate contained 29% (w/w) of 1,4-cyclohexanedione and 71% (w/w) of KCL.

Example 2

Synthesis of KCL monomer compound

[0071] Three further samples of KCL monomer were prepared with the same ingredients and according to the same process as described above in Example 1 with the sole exceptions being that in each sample : 0.17 M of 1,4-cyclohexanedione (herein sometimes referred to as "dione"); 150 ml of 1,2-dichloroethane was used; and that the reaction times were varied, as follows: in the first of these three additional samples (Sample 2A), the reaction was performed for 3 hours during which oxygen was added, in the second of these three additional samples (Sample 2B) the reaction was performed for 6 hours during which oxygen was added, and in the third of these three additional samples (Sample 2C) the reaction was performed for 16 hours during which oxygen was added.

[0072] In each sample, oxidation of dione was done at 40°C in the presence of 150 ml $ClCH_2CH_2Cl$ and PhCHO/[dione] = 3/1; $[dione]_0$ = 0. 17M.

[0073] Following reaction, the KCL produced thereby was then recovered and the quantity thereof determined by ^{1}H-NMR, as described above in Example 1. The results of these determinations are as follows :

Table 1

Sample	Time (in hours)	Conversion into KCL
Sample 2A	3	10%
Sample 2B	6	37%
Sample 2C	16	75%

[0074] The effect of the dione quantity placed in operation at the beginning of the reaction had been attributed to the bubbling therein of oxygen which limits the quantity of oxidant agent (perbenzoic acid) which is generated "in situ" (compare example 1 and 2B). A longer reaction time permits to increase the quantity of oxygen which is introduced into the reactor. However, the lactone concentration is thereof limited by its degradation into the reaction medium.

Example 3

Synthesis of KCL monomer compound

[0075] Two further samples of KCL monomer were prepared as follows: meta-Chloroperbenzoic acid (m-CPBA) having a purity of 70-75% (in peracid) was obtained (ACROS). This m-CPBA was washed with a phosphate buffer (pH = 7.5) until a filtrate having a pH = 7.5 was obtained. The residual peracid was then dried under reduced pressure for 48 hours at ambient temperature. (Vogel's, Textbook of Practical Organic Chemistry, 5th Edition, at page 457).

[0076] Analysis by gas chromatography revealed that this purified m-CPBA had a purity of greater than 99%. Gas chromatography was performed on a VARIAN STAR 3400 CX chramatograph equiped with a column DB5 of 30 m length (ID 032 mm, film 1 μm). m-CPBA was dissolved in dichloromethane.

[0077] 0.06 M of 1,4-cyclohexanedione (98% by weight) (ALDRICH), and 0.715 M of the purified m-CPBA (ACROS) were placed in a 500 ml reactor. Thereafter, 200 ml of commercial dichloromethane (99.5% w/w) (ACROS),

which had been dried over molecular sieves (ALDRICH) just before use was added to the reactor and the solution subjected to reflux for 16 hours at 40°C.

[0078] After evaporation of the solvent under reduced pressure, the precipitate was recovered, washed three times, each time with 250 ml of diethyl ether, filtered and dried under vacuum to a constant weight.

[0079] The recovered dried product was then weighted in order to calculate the yield of the 2-oxepane-1,5-dione (KCL) and the purity of the resulting KCL was determined by ^{1}H-NMR.

[0080] ^{1}H-NMR spectrum of the 2-oxepane-1,5-dione (KCL) obtained for determining purity was recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN400 superconducting magnetic system at 25°C.

[0081] A yield of about 56% (moles in comparison to the number of moles of the dione starting material) was calculated for the 2-oxepane-1,5-dione and the analysis by ^{1}H-NMR of the KCL product obtained, revealed a purity of the 2-oxepane-1,5-dione of about 90%.

Example 4

Synthesis of KCL monomer compound

[0082] Six further samples of KCL monomer were prepared as follows: meta-Chloroperbenzoic acid (m-CPBA) having a purity of 70-75% (in peracid) was obtained (ACROS). This m-CPBA was washed with a phosphate buffer (pH = 7.5) until a filtrate having a pH = 7.5 was obtained. (Vogel's, Textbook of Practical Organic Chemistry, 5th Edition, at page 457). The residual peracid was then dried under reduced pressure for 48 hours at ambient temperature.

[0083] For each sample, 19.8 mmol of 1,4-cyclohexanedione (98% by weight) (ALDRICH) and 22.6 mmol of the purified m-CPBA were placed in a 50 ml reactor. Thereafter, commercial dichloromethane (ACROS) (purity of minimum 99.5% by weight) which had been dried over molecular sieves (ALDRICH) just before use was added to the reactor in such a quantity to give the resulting solution of each sample the following concentrations of the 1,4-cyclohexanedione:

[0084] Sample 4A - 0.14 M; Sample 4B - 0.2 M; Sample 4C - 0.33 M; Sample 4D - 0.55 M; Sample 4E - 0.85 M; and Sample 4F - 0.99 M.

[0085] Thereafter, the solution of each sample was subjected to reflux for 4 hours at 40°C.

[0086] After evaporation of the solvent under reduced pressure, the precipitate was recovered, washed three times, each time with 40 ml of diethyl ether, filtered and dried under vacuum to a constant weight.

[0087] The recovered dried product was then weighted in order to calculate the yield of the 2-oxepane-1,5-dione. The results of the yield are as follows:

Table 2

Sample	Concentration	Yield
4A	0.14 M	47%
4B	0.2 M	54%
4C	0.33 M	56%
4D	0.55 M	60%
4E	0.85 M	58%
4F	0.99 M	58%

Example 5

Purification of KCL

[0088] 7.42 grams of KCL obtained as described above in Example 3, was placed into a 2 liter two-neck glass reactor which had been preheated under vacuum.

[0089] 1500 ml toluene (ACROS) (which had previously been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reactor via a capillary tube.

[0090] Two grams of CaH_2 were then introduced under agitation in the nitrogen atmosphere and the solution maintained under vigorous stirring at ambient temperature for 16 hours.

[0091] The solution was then filtered through a PYREX filter element (porosity : 17-40 micron) under a nitrogen atmosphere and transferred to another two liter reactor which had been preconditioned by heating under reduced pres-

sure.

[0092] The toluene (1000 ml) was then partially evaporated under a reduced pressure and thereafter recooled to 6°C for one night and the KCL becomes insoluble.

[0093] After being decanted, the residual solvent was eliminated under nitrogen agitation via a capillary tube. The KCL recovered was then dried at ambient temperature and under reduced pressure for 24 hours and recovered.

[0094] The recovered dried product was then weighted in order to calculate the yield of the 2-oxepane-1,5-dione (KCL), the purity of the resulting KCL was determined by ^{1}H-NMR and the melting point was determined using a capillary tube melting point apparatus (ELECTROTHERMAL 9100).

[0095] ^{1}H-NMR spectrum of the 2-oxepane-1,5-dione (KCL) obtained for determining purity was recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN400 superconducting magnetic system.

[0096] A yield of about 70% (weight in comparison to the weight of introduced KCl) was calculated for the 2-oxepane-1,5-dione and the analysis by ^{1}H-NMR of the 2-oxepane-1,5-dione (KCL) product revealed a purity of greater than about 98%.

[0097] Further, a melting point of about 110-112°C was determined for the KCL so obtained.

Example 6

Long-term stability of KCL monomer

[0098] KCL monomer, synthesized as described above in Example 3, was dried under reduced pressure for 24 hours.

[0099] A sample of the KCL monomer thus obtained was stored at ambient temperature in an air atmosphere and in natural light for three months. Another sample of the KCL monomer thus obtained was then stored at -20°C in nitrogen atmosphere for three months.

[0100] Following the storage period, each of the samples were analyzed by ^{1}H-NMR as was described above in Example 3 and by gas chromatography as was also described above in Example 3. These analyses revealed no signs of degradation of the KCL monomer of either sample.

Example 7

Homopolymerization of KCL

[0101] KCL, obtained as described in Example 1, was then polymerized in the presence of stannous octoate for producing PKCL.

[0102] A reaction tube equipped with a three-way stop cock and rubber septum on which was mounted a gas-exhaust valve was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0103] Thereafter, and under nitrogen atmosphere, the following was added to the reaction tube : 2.5 mmol of KCL obtained as described above in Example 1; 1 ml of 0.05 M $Sn(Oct)_2$ (TEGOKAT 129, TH.GOLDSMITH AG) obtained as provided by supplier in toluene (ACROS) (which had previously been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reactor via a capillary tube.

[0104] The reaction tube was then maintained under stirring in an oil bath at about 100°C. After 16 hours the reaction was stopped. The polymer PKCL was recovered from the reaction milieu by filtration on paper and washed liberally with methanol. The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of PKCL (in relation to the weight of the monomer is of about 95 %).

[0105] The PKCL obtained as described above was then characterized by ^{1}H-NMR (as described above in Example 1), DSC (using a Dupont 910 Differential Scanning Calorimeter thermal analyzer calibrated with Indium and following the manufacturer's instructions) and thermogravimetric analysis (TGA) performed under nitrogen with a Dupont TGA 51 thermogravimetric analyzer (heating rate = 10°C/minute).

[0106] DSC analysis revealed that the PKCL so obtained possessed a particularly high melting point (T_M) of about 156°C (ΔH_m =90 J/g) and a glass transition temperature (T_g) of about 32°C.
TGA analysis revealed a 5% (w/w) loss at a temperature of about 198°C. The decomposition temperature was determined to be about 220°C.

Example 8

Homopolymerization of KCL

[0107] In a reaction tube equipped with a three-way stop cock and rubber septum was introduced 0.8 grams of

KCL, obtained as described above in Example 3. 1.25 ml of a 0.05 M solution of $Sn(Oct)_2$ (TEGOKAT 129, Th. Goldschmidt AG) in toluene (which was previously dried on CaH_2 and distilled) were placed in the reaction tube. The toluene was then evaporated under reduced pressure.

[0108] The reaction tube was maintained under agitation in an oil bath maintained at 100°C. After 2 hours, the reaction was stopped. The PKCL was recovered by filtration on paper and washed liberally with methanol.

[0109] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of PKCL (in relation to the weight of the monomer) is of about 98%. The PKCL obtained was found to possess a high melting point (T_M) of about 156°C and a glass transition temperature (T_g) of about 35°C.

Example 9

Homopolymerization of the KCL

[0110] A reaction tube equipped with a three-way stop cock and rubber septum was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0111] Thereafter, and in nitrogen atmosphere, 0.6 grams of purified KCL, obtained as described above in Example 5, 0.1 ml of a 0.08 M solution of $Sn(Oct)_2$ (TEGOKAT 129, TH.GOLDSMITH AG) and 0.9 ml of toluene (ACROS) (which had previously been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reactor via a capillary tube.

[0112] The reaction tube was maintained under agitation in an oil bath maintained at 90°C. After 6 hours, the reaction was stopped. The PKCL which had precipitated in the milieu was recovered by filtration on paper and washed liberally with methanol (LAB CHEMISTY 1340 assay: 99% by weight) as received from the supplier.

[0113] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of PKCL (in relation to the weight of the monomer) is of about 90%.

Example 10

Characterization of PKCL by Wide Angle X-ray Scattering (WAXS)

[0114] Samples of PKCL obtained using the TOSUO monomer (obtained as described in Macromolecules 1997, 30, 406-409) and using the PKCL polymer obtained as described above in Example 7, were analyzed by WAXS.

[0115] Powder WAXS diagrams were recorded with diffractometer having a Philips goniometer PW1050 equipped with a graphite monochromator located behind the receiving slit, a Philips generator PW 1130 (40 kV-20mA, Ni-filtered Cu Kα radiation at λ = 1.5418 Å) and Philips Proportional Detector PW 1352.

[0116] The results of this analysis revealed that the PKCL produced starting from both monomers had three principle peaks with intensities relative to 100/40/10 were detected at 4.1, 3.4 and 2.8 Å, respectively, for the PKCL obtained starting from TOSUO and at 4.1, 3.4 and 2.8 Å, respectively, for the PKCL obtained starting from KCL.

Example 11

Copolymerization with ε-CL

[0117] KCL, obtained as described in Example 1, was then co-polymerized with ε-CL in the presence of stannous octoate for 16 hours at 100°C producing an P(KCL-ε-CL) copolymer having KCL molar fraction of 0.29.

[0118] A reaction tube equipped with a three-way stop cock and rubber septum was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0119] Thereafter, under nitrogen atmosphere, 2 mmol of the KCL (obtained as described above in Example 1), 3.6 mmol of ε-CL (ACROS) (which had been dried by refluxing over CaH_2 and distilled under reduced pressure just before use), 0.1 ml of a 0.05 M solution of $Sn(Oct)_2$ (TEGOKAT 129, TH.GOLDSMITH AG) in 0.9 ml of toluene (ACROS) (which had previously been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reactor via a capillary tube, so that the KCL molar fraction f_{KCL} in the comonomer feed equals 0.36.

[0120] The reaction tube was the maintained under stirring in an oil bath at about 100°C. After 16 hours the reaction was stopped. The copolymer was recovered from the reaction milieu by precipitation in methanol (LAB CHEMISTY 1340 assay: 99% by weight) as received from the supplier.

[0121] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of(P(KCL-ε-CL) (in relation to the weight of the monomers) is of about 92 %.

[0122] The P(KCL-ε-CL) obtained as described above was then characterized by ^{1}H-NMR (as described above in Example 1), Size-exclusion Chromotography (SEC) (performed in THF by using Hewlett-Packard 1090 liquid chromo-

tography equipped with a Hewlett-Packard 1037 A refractometer index detector and using the protocol described in Macromolecules, 1997, 30, 1947-1954), DSC (using a Dupont 910 Differential Scanning Calorimeter thermal analyzer calibrated with Indium and following the manufacturer's instructions) and thermogravimetric analysis (TGA) (performed under nitrogen with a Dupont TGA 51 thermogravimetric analyzer (heating rate = 10°C/minute).

[0123] ^{1}H-NMR revealed a KCL molar fraction f_{KCL} in the copolymer of 0.29. The P(KCL-ε-CL) copolymer was also found to have a number average molecular weight of about 5200 and a polydispersity index of 2.6, as determined by SEC. The P(KCL-ε-CL) copolymer was further found to possess two melting points (T_M) of about 77°C and about 90°C and a glass transition temperature (T_g) of about 3°C, as measured by DSC.

Example 12

Copolymerization with ε-CL

[0124] A reaction tube equipped with a three-way stop cock and rubber septum was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0125] Thereafter, in nitrogen atmosphere, 0.32 grams of purified KCL (obtained as described above in Example 5) was added to the reaction tube. 0.52 grams of ε-CL (ACROS) (which had been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reaction tube via a hypodermic syringe which also had been preconditionned three times (under vacuum with the aid of a Bunsen burner).

[0126] Furthermore, 4.6 ml of a 0.003 M solution of $Sn(Oct)_2$ (TEGOKAT 129, TH.GOLDSMITH AG) in 0.9 ml of toluene (ACROS) (which had previously been dried by refluxing over CaH_2 and distilled under reduced pressure just before use) was then added to the reactor via a capillary tube was then added to the reaction tube, also by hypodermic syringe.

[0127] The toluene was then evaporated under reduced pressure and the reaction tube maintained for four hours under agitation in an oil bath at 120°C. After 4 hours, the reaction was stopped. The viscous solution obtained was then diluted by 2 ml of tetrahydrofuran (99% by weight purity) (ACROS). The PKCL was then precipitated in 20 ml of cold methanol (LAB CHEMISTY 1340 assay: 99% by weight) as received from the supplier.

[0128] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of P(KCL-ε-CL) (in relation to the weight of the monomers) is of about 84 %.

Example 13

Copolymerization with ε-CL

[0129] Three further P(KCL-ε-CL) copolymers have been prepared as described above in Example 11 with the exception of the quantities of the KCL, ε-CL and $Sn(Oct)_2$ above which quantities are given in Table 3 below.

[0130] These copolymers were then recovered and analyzed, as was also described above in Example 12. The results of these analyses are given below in Table 3:

Table 3

KCL quantity	ε-CL quantity	$Sn(Oct)_2$ 0.05M quantity	Yield	F_{KCL}	Tg	Tm
0.294 g	0.3 ml	1 ml	85%	0.41	6°C	78°C and 94°C
0.183 g	0.125 ml	0.5 ml	95%	0.50	9°C	86°C and 103°C
0.467g	0.15 ml	1 ml	88%	0.77	5°C	96°C and 132°C

Example 14

Copolymerization with ε-CL

[0131] A reaction tube equipped with a three-way stop cock and rubber septum was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0132] Thereafter, in nitrogen atmosphere, 0.06 grams of purified KCL (obtained as described above in Example 5) was added to the reaction tube. The KCL monomer was purified 3 times by azeotropic distillation with (3 × 7 ml) toluene (previously dried on CaH_2 and distilled under reduced pressure). 0.52 grams of ε-CL (ACROS), which had been previously dried on CaH_2 and distilled under reduced pressure, was then added to the reaction tube via a hypodermic

syringe which also had been preconditionned three times (under nitrogen atmosphere) with the aid of a Bunsen burner).

[0133] 3 ml of toluene (which was previously dried on CaH_2 and distilled) were placed in the reaction tube which was maintained for 10 minutes under agitation in an oil bath at 90°C.

[0134] 0.4 ml of a 0.11 M solution of $Al(OiPr)_3$, which had been previously twice sublimated and then dissolved in toluene (which was previously dried on CaH_2 and distilled) under nitrogen, was then added to the reaction tube, also by hypodermic syringe.

[0135] The reaction tube was maintained for four hours under agitation in an oil bath at 90°C. After 4 hours, the reaction was stopped. The viscous solution obtained was then diluted by 2 ml of tetrahydrofuran (ACROS). The copolymer was then precipitated in 20 ml of cold methanol (Lab Chemistry, 99 %).

[0136] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of the P(KCL-ε-CL) (in relation to the weight of the monomers) is of about 97 %.

Example 15

Copolymerization with ε-CL

[0137] A reaction tube equipped with a three-way stop cock and rubber septum was preconditioned three times (under vacuum with the aid of a Bunsen burner).

[0138] Thereafter, in nitrogen atmosphere, 0.32 grams of purified KCL (obtained as described above in Example 5) was added to the reaction tube. 0.52 grams of ε-CL (ACROS) which had been previously dried on CaH_2 and distilled under reduced pressure, was then added to the reaction tube via a hypodermic syringe which also had been preconditionned three times (under vacuum with the aid of a Bunsen burner).

[0139] 2 ml of a 0.003 M solution of $Sn(Oct)_2$ (TEGOKAT 129, Th. Goldschmidt AG) and 0.25 ml of a 0.06 M of 1-phenyl-2-propanol (SIGMA-ALDRICH; assay : 98 %) in toluene (in both case toluene was previously dried on CaH_2 and distilled) were added to the reaction tube by hypodermic syringe.

[0140] The toluene was then evaporated under reduced pressure and the reaction tube maintained for one hour under agitation in an oil bath at 120°C. After 4 hours, the reaction was stopped. The viscous solution obtained was then diluted by 2 ml of tetrahydrofuran (ACROS). The copolymer was then precipitated in 20 ml of cold methanol (Lab Chemistry, 99 %).).

[0141] The polymer obtained in this manner was then dried under vacuum to a constant weight. The yield of the P(KCL-ε-CL) (in relation to the weight of the monomers) is of about 84 %.

[0142] While specific embodiments of the present invention have been shown and described to illustrate the inventive principles herein, it is to be understood that this is only meant to be illustrative and not limiting of the invention disclosed herein.

Claims

1. A compound useful as a monomer for the production of polymers characterized in that the compound is a cyclic esterketone

2. The compound according to claim 1, further characterized in that the cyclic esterketone is 2-oxepane-1,5-dione.

3. A process for the synthesis of a monomer compound characterized by the oxidation of 1,4-cyclohexanedione.

4. The process according to claim 3, further characterized in that the monomer compound is 2-oxepane-1,5-dione.

5. The process according to any of claims 3-4, further characterized in that the 1,4-cyclohexanedione is oxidized by a peracid.

6. The process according to claim 5, further characterized in that the peracid is perbenzoic acid.

7. The process according to claim 5, further characterized in that the peracid is a chloroperacid.

8. The process according to either of claims 6 or 7, further characterized in that the chloroperacid is chloroperbenzoic acid.

9. The process according to claim 8, further characterized in that the chloroperbenzoic acid is meta-chloroperbenzoic

acid.

10. The process according to any of claims 3-4, further characterized in that the 1,4-cyclohexanedione is oxidized by an aldehyde.

11. A cyclic esterketone compound useful as a monomer for the production of polymers characterized in that the compound is obtainable by the process of any of claims 3-10.

12. A process for the preparation of PKCL characterized by the polymerization of 2-oxepane-1,5-dione.

13. The process according to claim 12, wherein the 2-oxepane-1,5-dione is polymerized with at least one other monomer.

14. The process according to claim 13, wherein the at least one other monomer includes ε-CL.

15. The process according to any of claims 13-14, wherein the PKCL copolymer have about 5% to about 80% (w/w) KCL.

16. A PKCL polymer obtainable by the polymerization process of any of claims 12-15.

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number EP 99 20 1957

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	J.OUAZZANI-CHAHDI: "PREPARATION OF BOTH ENANTIOMERS OF A CHIRAL LACTONE" TETRAHEDRON LETTERS., vol. 28, no. 10, 1987, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM., NL, pages 1109-1112, XP002124689 * page 1109 - page 1110 *	1,3,5-9	C07D313/04 C08G63/08
A	US 3 418 290 A (A.BANTJES) 24 December 1968 * column 1 - column 5 *	1,12-16	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C07D
C08G

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
THE HAGUE	6 December 1999	FRANCOIS, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 99 20 1957

Claim(s) searched completely:
2-16

Claim(s) searched incompletely:
1

Reason for the limitation of the search:

Present claim 1 relate to an extremely large number of possible compounds. Support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claim 1 so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claim 1 which appear to be supported and disclosed, namely those parts relating to the oxepan-one, -dione compounds.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 20 1957

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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06-12-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3418290 A	24-12-1968	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82