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(71) Applicants
Enoxy Chimica SpA
(Italy),
Via Mille 9/C Sassari,
Italy
(72) Inventors
Arnaldo Roggero
Luciano Gargani
Mario Bruzzone
(74) Agent and/or
Address for Service
Haseltine, Lake and Co.,
Hazlitt House,
28 Southampton
Buildings,
Chancery Lane,
London WC2A 1AT

(54) Aromatic - diene - pivalolactone
block copolymer

(57) Block-copolymers of the A-B-C pattern wherein A is an alphasubstitutedstyrene, vinylbiphenyl, isopropenylbiphenyl, vinylnaphthalene or isopropenyl-naphthalene block, B is a diene block or a hydrogenated diene block and C is a pivalolactone block are prepared by sequentially polymerising first A and then B to form a lining AB block copolymer, reacting this with CO₂ to form a carboxyl function, and reacting pivalolactone with the carboxyl-functional AB copolymer.

Fig.1

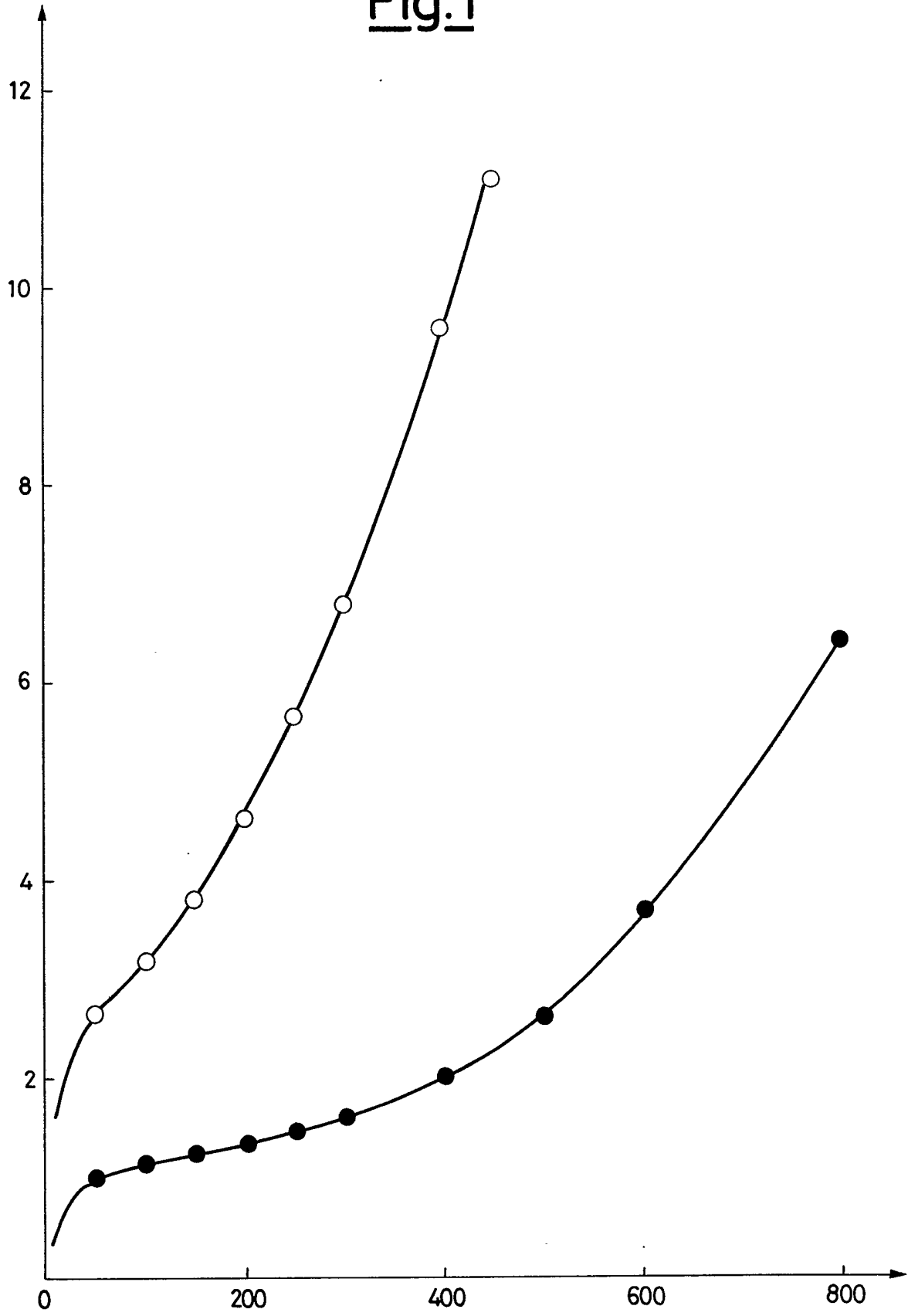


Fig. 2

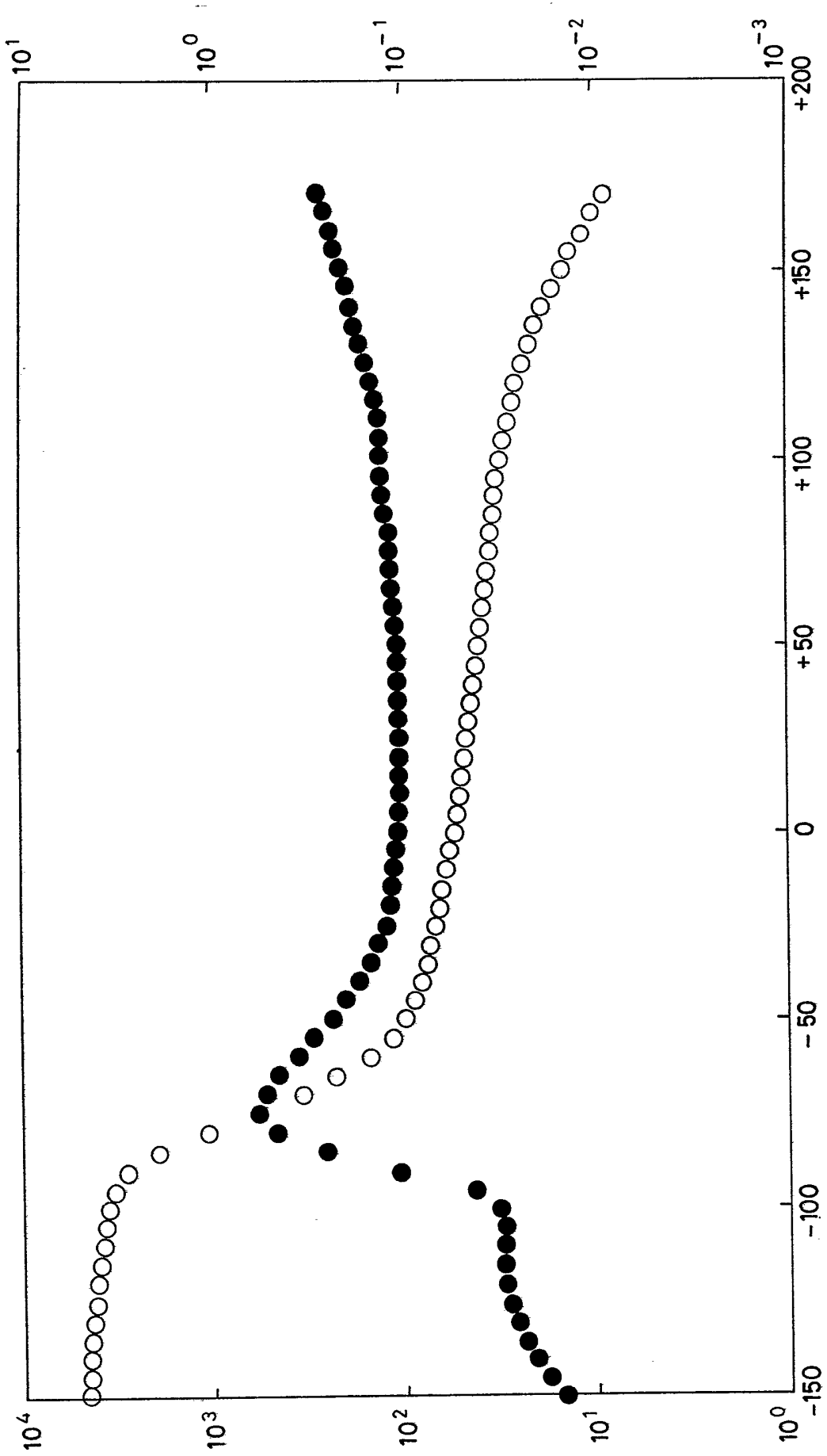
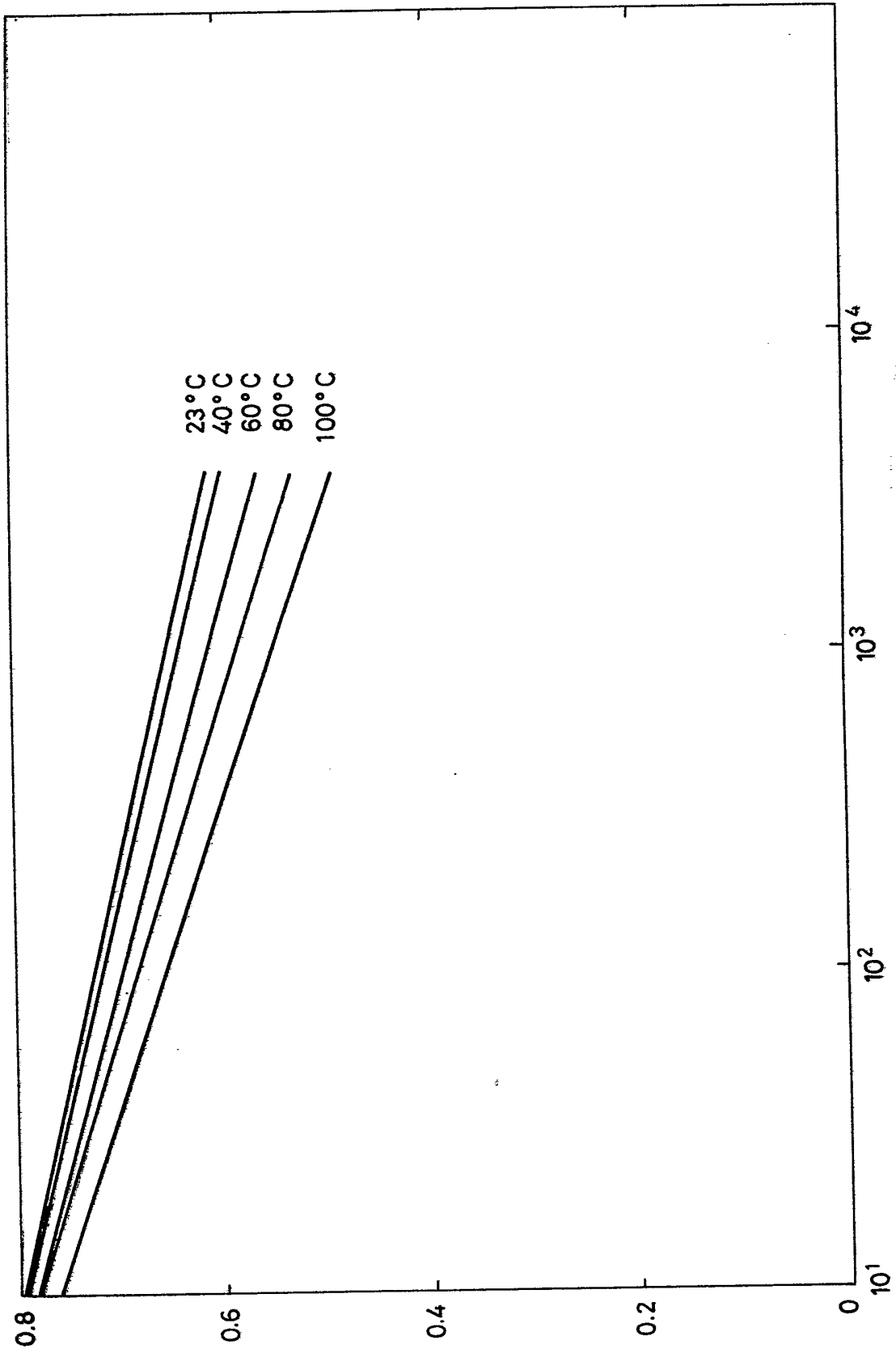


Fig. 3



SPECIFICATION

Block-copolymers based on pivalolactone and process for their preparation

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The possibility is known of synthesizing block copolymers of the A-B-C pattern in which A is styrene, B is a diene and C is a pivalolactone (US Pat. 3,557,255).

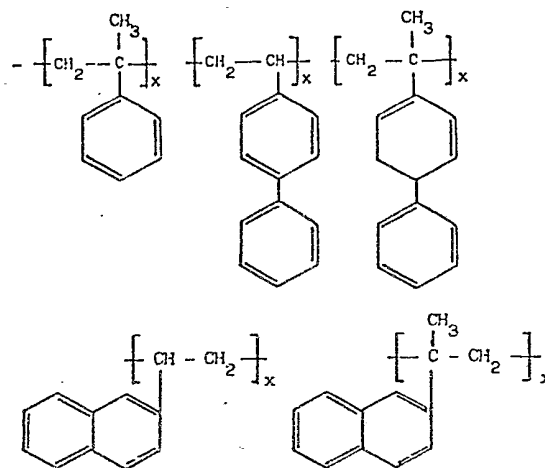
- 10 These polymers have thermoelastomeric properties and exhibit properties which are dependent on their biphasic nature (hard and soft). The product which exhibit a fair separation of the two phases and a satisfactory interaction between the domains of the
- 15 hard phases (two equal phases in the polymers of the ABA pattern, two different phases in the polymers of the ABC pattern) exhibit satisfactory features. Also the transition temperature of the "hard" blocks is a significant parameter in the sense that the higher
- 20 transition temperatures generally enable the polymers to exhibit their properties at higher temperatures.

- The ABC products claimed in US Pat. 3,557,255 have definite properties which are, however, limited
- 25 to the transition which is too low for the glassy (vitreous) hard phase A (about 90°C) of the polystyrene blocks.

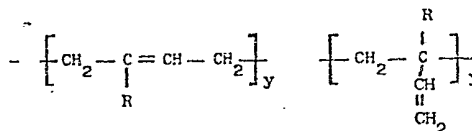
- An objective of this invention is the synthesis of products in which the C block, for its being a high-
- 30 melting-point crystalline hard phase (values comprised between 160°C and 230°C consistently with the segmental length) and the block B, for its being a "soft" phase of the diene type (also hydrogenated),
- A can be an amorphous and/or crystalline phase having a high transition temperature (vitreous or glassy)
- 35 equal to or higher than 140°C so as to provide the opportunity of obtaining thermoelastomeric products having improved properties. The products obtained according to the present invention are
- 40 block copolymers of the A_xB_yC_z pattern wherein A is a sequence of aromatic polyvinyl and/or polyisopropenyl, with the exclusion of styrene, B is a polydiene sequence and/or a hydrogenate derivative thereof, and C is a polypivalolactone sequence. x, y
- 45 and z are integers which represent the monomeric units in the several sequences.

The structures of the several sequences can be represented by the following formulae:

Sequence of the A pattern:

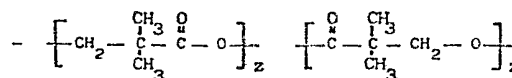


and the different possible isomers thereof.
Sequences of the B pattern:



wherein R is -H or -CH₃.

Sequences of the C pattern:



- 50 As a function of the different values, x, y and z, one obtains products having different technological properties.

- More particularly, the value of z can even be very small and arrive just to a few units only (greater than or equal to 5). The compounds are prepared by a stepwise process to be summarized diagrammatically as follows:

STAGE 1

- This first stage provides for the polymerization of
- 60 the vinylaromatic monomer referred to above with or without an apolar solvent and/or co-solvent (polar, to be added but in the subsequent stage of Stage 2, if it is desired to obtain the polydiene block with a predominant 1-4 structure) being present. The
- 65 reaction pattern can be resumed as follows:
sec. Butyl-Li + n-alphamethylstyrene → sec. butyl-(alphamethylstyrene)_xLi.

- It should be considered, moreover, that the polymerization of alphamethylstyrene is an equilibrium polymerization which is a function both of concentration and temperature and that x is equal to or smaller than n.

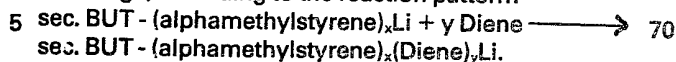
Certain of the chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

This print takes account of replacement documents later filed to enable the application to comply with the formal requirements of the Patents rules 1978.

STAGE 2

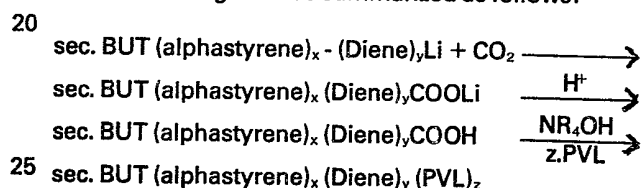
The second stage provides for the addition of the diene to the product which has been formed in the first stage, according to the reaction pattern:



The addition of the diene must be carried out during the initial steps of this second stage cautiously so as to prevent the depolymerization of the first block (as a consequence of the dilution) and to arrive at a final condition (thorough conversion of the diene) in which the stirring of the solution is satisfactory in order to be able to perform the following stage. In addition, the "liveliness" of the polymer must not have been jeopardized. The microstructure of the diene is conditioned by the presence of polar activators or by its absence.

STAGE 3

The third stage can be summarized as follows:



This procedure permits to perform the addition of the pivalolactone block (C) to the AB-COOH polymer which has been homogeneously functionalized in a well defined manner with considerable advantages over the procedure disclosed in the US Pat. 3,557,255.

The synthesis of the products of the present invention will now be described in a more detailed fashion.

1) SYNTHESIS OF THE "A" SEQUENCE

Consistently with the type of monomer which is employed, the polymerization step is carried out with or without a solvent being present, with or without the use of polymerization activators, having in mind the kind of product that one desired to obtain.

In the case of alphamethylstyrene, for instance, the polymerization step is preferably carried out as a bulk polymerization at room temperature or, in solution, at a lower temperature.

As the initiators, alkali metal alkyls, their amides and hydrides can be employed.

The initiator which is customarily used is Li-sec.butyl but also ethyl-lithium, nor.propyl-lithium, isopropyl-lithium, tert.butyl-lithium and sodium-amyl can be adopted.

The use, or not, of aliphatic, cycloaliphatic, aromatic and alkyl aromatic solvents, apolar solvents, aprotic solvents, which enable a "living" polymerization of the monomers aforesaid to be carried out, can be conditioned by the value of the T_c temperature of the latter, T_c being their "ceiling" temperature, which is characteristic for each individual monomer and is the temperature above which a certain monomer cannot any more be converted into a polymer.

Also the polymerization temperature for the different compounds which are employed is conditioned by their T_c value; as a rule, the working

temperature range is between -80°C and $+150^\circ\text{C}$ and the range -30°C to $+80^\circ\text{C}$ is preferred.

The kinds of monomers are selected from among the vinyl compounds (styrene excluded) and the alkenylaromatic compounds. More particularly, there are used: alphamethylstyrene, vinylbiphenyl, isopropenylbiphenyl, vinylnaphthalene and isopropenyl-naphthalene, the several possible isomerides being included. The degree of polymerization, which can be obtained at leisure (living polymer) is selected consistently with the kind of product one desires to obtain so as to have any desired ratio of the HARD phase to the SOFT phase (see following item 2).

2) SYNTHESIS OF THE "B" SEQUENCE

The diene is added to the living polymer of the previous paragraph with the counter-ion Li, Na, or K, consistently with the kind of initiator which is used, and one obtains the AB block wherein the diene structure is influenced by the type of counter-ion and the kind of solvent used.

The addition must be made under such conditions as not to modify the living nature of the block A and the monomer-polymer balance of the same block A (whenever A consists of monomers having low T_c values).

When no chain-ending substances is present, the polymerization of the diene can be thoroughly completed, and all the diene is incorporated into the polymer.

The molecular weight of the B sequence is proportional to the relative quantity of the diene monomer and the number of living A chains which are present in the system.

Generally speaking, aliphatic, cycloaliphatic, aromatic and alkyl aromatic, apolar and aprotic solvents are used.

Whenever the A sequence consists of monomers having low T_c values, as outlined above in the initial clause of this paragraph, prior to diluting with a solvent, a blocking reaction is to be caused to occur, for example for blocking the polymethylstyrene terminal with butadienes so as to prevent the monomer-polymer equilibrium from being shifted towards the monomer due to the dilution. Subsequently, one may proceed with the dilution without impairing the satisfactory outcome of the polymerization run. As a rule, the operative temperature range is from -50°C to $+150^\circ\text{C}$, the range from 0°C to 60°C being preferred.

The dienes which are generally employed are those which contain up to 12 carbon atoms and they preferably are 1,3 - butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, 1,3 - pentadiene (piperylene), 2 - methyl - 3 - ethyl - 1,3 - butadiene, 3 - methyl - 1,3 - pentadiene, 1,3 - hexadiene, 2 - methyl - 1,3 - hexadiene and 3 - butyl - 1,3 - octadiene.

3) SYNTHESIS OF THE "C" SEQUENCE

Starting from the living AB polymer as obtained in stage 2):



Products are obtained in which the distribution of the pivalolactone segments throughout all the

chains of the AB type is achieved quite homogeneously.

The functionalization of the AB polymer by carboxyl groups according to the equation i) is carried out by contacting the living polymer AB with a large excess of CO₂ dissolved in aliphatic and/or cycloaliphatic solvents and working at a temperature comprised between -50°C and +20°C, the preferred range, however, being between -5°C and +5°C for a time of a few hours.

The carboxyl function is set free by a treatment with Brönsted acids.

The polymer thus obtained can be used as such in the subsequent grafting stage (see hereinafter) of the pivalolactone block, but it can be hydrogenated beforehand. In the latter case, if the diene is butadiene, its structure must properly be selected so as to obtain, upon hydrogenation, well defined elastomeric products. The product of the reaction i), dissolved in tetrahydrofuran or/and admixtures of it with aromatic, aliphatic and cycloaliphatic solvents, is caused to interact with tetraalkylammonium bases of the kind NR^IR^{II}R^{III}R^{IV}OH wherein R^I, R^{II}, R^{III} and R^{IV}, equal to or different from each other are alkyl radicals having from C1 to C8, the ratio COOH/base being comprised between 1:0.5 and 1:1, at room temperature for a few minutes.

The addition of pivalolactone (sequence iii) in variable amounts consistently with the kind of product one desires to obtain, takes place with quantitative yields when working at temperatures comprised between +20°C and +60°C for a few hours. By so doing, an even distribution of PVL (pivalolactone units) throughout all of the polymeric chains can be achieved.

EXAMPLES

All the operative details will become fully apparent from the scrutiny of the following examples.

These examples, however, shall not be construed as limitations of the subject invention.

EXAMPLE 1

A glass tubular reactor, sealtight and having a volume of about one liter and equipped with a stirrer, nitrogen inlet, pressure and temperature gauges and a reactant charging inlet, is charged with 50 mls of alphasethylstyrene and 0.65 millimol of Li-sec.butyl. The polymerization lasts 1 hour and 45 minutes at room temperature, whereafter 2 g of butadiene are introduced and the reaction is allowed to proceed, still at room temperature, for 15 additional minutes. There are then introduced 300 mls of cyclohexane and 34 g of butadiene, the reaction being allowed to proceed at 60°C during one hour. On completion of the reaction, the polymeric solution thus obtained is slowly transferred into a nitrogen-filled reactor containing 200 mls of CO₂-saturated cyclohexane (in a stream of the latter gas) at 0°C. After one hour, the mass is treated with HCl, then washing to neutrality and precipitating with methanol the functionalized product (50 g) which shows (H.NMR analysis from CDCl₃) the following composition:

alphamethylstyrene (alphaSTY) = 28% by weight (15.2% molar)

Butadiene (BUT) = 72% by weight (1-2 fractions =

9% molar)

1-4 fractions = 75.8% molar

Its molecular weight is 77,000 g/g mol.

During the second step 47 g of the latter polymer are dissolved in 250 mls of toluene and 250 mls of tetrahydrofuran (THF) adding 0.5 milliequivalents of tetrabutylammonium hydroxide (T.B.A.I.) and interaction is allowed to go ahead for 15 minutes at 60°C. Lastley, pivalolactone (PVL, 3 mls) is charged and the reaction is allowed to proceed at the same temperature for 3 additional hours. By addition of a few mls of hydrochloric acid and precipitation with methanol, 50 g of a product are isolated, having the following composition:

PVL = 6% by weight; alphaSTY = 28% by weight and BUT = 66% by weight.

The differential thermal analysis displays three transitions, at -87°C, at +150°C - + 160°C and at +207°C (melting) which can be attributed, respectively, to polybutadiene having a high degree of cross-linking 1-4 (sharp transition), to polyalphaSTY (not well defined) and to poly PVL (sharp transition). The samples for the technological tests have been cut out of plates which have been compression moulded between two aluminium plates treated with a silicon mold-release agent. The moulding conditions can be summarized as follows: Temperature 240°C - Pressure 30 kg/cm² - Preheating 10 minutes - Moulding 10 minutes - Cooling by running water at ambient temperature, which produces a maximum cooling rate (initially) of 40°C per minute. The pressure is released as the temperature has dropped to 30°C.

The samples for the tensile tests have been cut with a cutting die DIN S 3 A out of a 1 mm thick plate. The tensile tests have been carried out with an INSTRON testing machine according to the DIN 53504 Standard at a speed of 200 mm a minute. The lead has been read out at elongation intervals of 50%. The resulting plot has been identified by the symbol 1 in Figure 1.

The thermodynamic and mechanical behaviour has been tested with a RHEOVIBRON DDV II viscoelastomer made by TOYO INSTRUMENTS at the frequency of 110 cycles per second (Hertz, Hz) with a heating rate of 2°C a minute. The control of the temperature has been made with a gas thermostat (nitrogen) by T.N.O. which gives an accuracy as high as ± 0.2°C.

The thermodynamic and mechanical performance is resumed in Figure 2. The glassy transition (peak of the loss factor tan delta) at -74°C is evident and is characteristic of the polybutadienes having a contents of vinyl units of less than 15%. Such a microstructure of the elastomeric constituent warrants for the resilient behaviour of the material down to very low temperatures such as -30°C.

At the opposite end, the beginning of the transition of the poly-alphasethylstyrene becomes appreciable in the neighbourhood of -100°C, becoming more and more conspicuous. The tests are discontinued at +170°C due to the collapse of the sample: such collapse takes place at about +90°C in the commercial styrene-butadiene-styrene copolymers.

The area of relative constancy of the modulus of

elasticity E' is spread from about -30°C to about $+120^{\circ}\text{C}$, and this fact is a remarkable improvement over the styrene-based copolymers which show a decay at temperatures which do not exceed 80°C .

5 The measurements of stress release under deformation have been carried out with an INSTRON tester on circular samples having a diameter of 16 mm and a thickness of 6 mm.

10 The 25% deformation has been applied by compression at the speed of 50 mm/minute. The drop of the stress as a function of time has been plotted in Figure 3 for several testing temperatures (the measurements have been taken by using the INSTRON conditioning chamber). The retention of the elasticity properties as a function of time and temperature is definitely lower than that which is shown by the styrene-butadiene-styrene block copolymers. More particularly, the stress drop at 100°C is slower with respect to the SBS copolymers at 40°C .

20 Figure 1 reports a plot having at the ordinates the stress σ , expressed in MPa, and at the abscissae the deformation ϵ , expressed in percentage. There can be seen the trends of the samples of Example 1 (o) and those of Example 2 (o).

25 Figure 2, in practice, shows the dynamic-mechanical pattern of the sample of Example 1. The abscissae are the temperature scale, T, expressed in degree centigrade ($^{\circ}\text{C}$). The ordinates at the left hand show the logarithmic scale of the moduli of elasticity E' , expressed in MPa (o). The ordinates on the right side show the logarithmic scale of the loss factor $\tan \delta$, an adimensional magnitude (o).

30 Figure 3 shows a plot having at the ordinates the normalized stress $\sigma t/\sigma_0$, which is adimensional and at the abscissae there is the logarithmic scale of the time, t, expressed in seconds: the plot shows the behaviour of the sample of Example 1.

EXAMPLE 2

40 In the reactor described hereinabove there are charged 50 mls of alpha-STY and 0.75 millimol of Li-sec.butyl, and polymerization is carried out for 1 hour and 15 minutes at room temperature. There are then introduced 4 g of butadiene and, after 5 minutes, 350 mls of cyclohexane and 25 g of butadiene, the polymerization being then carried out during 1 hour at 60°C .

The procedure is then the same as in Example 1 and there are isolated 43 g of COOH-functionalized polymer having the following characteristics:

50 alphaSTY: 32.5% by weight (18.2 molar %) – BUT: 67.5% by weight (1-2 fraction 9 molar %, 1-4 fraction 72.8 molar %), mol weight measured by G.P.C. is 56,000 g/gram.mol. Such a polymer, dissolved like the previous one in the toluene/THF (tetrahydrofuran) mixture (proportions 1:1 by volume) is treated with 0.48 milliequivalents of T.B.A.l. (reaction for 15 minutes at 60°C) and 2 mls of PVL (reaction for 2 hours at 60°C). There are isolated with the procedure described above 45 g of a product which has the following composition: PVL: 4.0% by weight – alphaSTY: 31% by weight and BUT: 65% by weight.

The differential thermal analysis exhibits the expected transitions at -87°C (BUT), at $+150^{\circ}\text{C}$ – $+160^{\circ}\text{C}$ (alphaSTY), and at 197°C (PVL).

55 The tensile properties of this product are shown

with the symbol 2 in Figure 1. Also this product shows a widening of rubbery behaviour area, both on the temperature scale and the time scale, as compared with the commercial styrene-butadiene-styrene copolymers.

EXAMPLE 3

70 In the reactor described hereinabove there are charged 200 mls of nor.heptane, 12 g of alphaSTY and 0.5 millimol of Li-sec.butyl. The polymerization step is carried out at -78°C for 3 hours. There are then added 28 g of isoprene (IP) with 100 mls of nor.heptane and the temperature is gradually allowed to rise to ambient temperature, whereafter polymerization is carried out at 60°C for 2 hours. On completion of the polymerization step, the viscous polymer is siphoned out into a nitrogen-filled reactor containing nor.heptane which has been saturated with gaseous carbon dioxide (anhydrous) and, by adopting the usual procedure, there are isolated 40 g of a functionalized product having the following composition: (^1H NMR from CDCl_3): alpha-STY 30% by weight (19.8 molar%), IP: 70% by weight (3-4 fractions: 8.0% molar, and 1-4 (or 4-1) fractions: 72.2 molar %).

90 The molecular weight, as determined by GPC is 84,000 g/gram.mole and 40 g of this polymer are dissolved in the usual solvent mixture and treated, at the outset, with T.B.A.l. (0.4 milliequivalent) and subsequently with PVL (2.5 g). There are obtained, by operating as described above, 42.5 g of a polymer having the following composition: PVL: 5.9% by weight; alphaSTY: 28.2% and IP: 65.9% by weight.

The Differential Thermal Analysis clearly shows the transitions which can be attributed to polyisoprene (-68°C), polyalphaSTY ($+150^{\circ}\text{C}$ – $+165^{\circ}\text{C}$) and poly PVL ($+209^{\circ}\text{C}$).

EXAMPLE 4

105 The apparatus described hereinabove is charged with 50 mls of cyclohexane and 0.5 millimol of Na.nor.butyl - tetramethyl - ethylenediamine (TMEDA) in a cyclohexane. Polymerization is caused to occur at the temperature of $+5^{\circ}\text{C}$ for about one hour and 2 g of butadiene are subsequently added and the reaction is allowed to proceed for 5 minutes at the same temperature ($+5^{\circ}\text{C}$). Then there are charged 26 g of butadiene in 300 mls of cyclohexane and the polymerization is carried out for one hour at 60°C .

110 On completion of the polymerization step, the functionalization with CO_2 is effected and there is obtained a alphaSTY: 30% by weight – BUT: 70% by weight (the 1-2 structure predominates). Its molecular weight is 92,000 g/g.mol (via G.P.C.). Then, the procedure is the same as described above by treating with T.B.A.l. (0.4 milliequivalent) and PVL (3 mls). There are isolated 43 g of a polymer having a contents of alphaSTY of 28% by weight, BUT 65% by weight and PVL 7% by weight.

125 The Differential Thermal Analysis (DTA) exhibits the transitions of the high-vinyl polybutadiene (about -30°C), of the alphaSTY (not very sharply defined) in the area $+150^{\circ}\text{C}$ – $+160^{\circ}\text{C}$ and poly PVL (sharply defined) at $+207^{\circ}\text{C}$.

EXAMPLE 5

130 The test of Example 4 is repeated with the only dif-

ference that the solvent is diethylether utilizing K-cumyl in the same proportions as in the previous example. The results are comparable.

EXAMPLE 6

- 5 A solution of 6 g of p.vinylbiphenyl in 150 mls of cyclohexane is supplemented with 0.3 millimol of Li.sec.butyl and the polymerization is carried out for 3 hours at a temperature of 60°C. On completion of this step there are introduced 14 g of butadiene and
10 the polymerization is carried out for one additional hour, at 60°C again. The polymer is functionalized with CO₂ operating as described above. A product is isolated, 20 g, the composition of which (¹H NMR from CDCl₃) is: p.vinylbiphenyl: 30% by weight (11.4 molar %)- BUT: 70% by weight (1-2 structure 8.9 molar % - 1-4 structure 79.7 molar %). Its molecular weight (from GPC) is 75,000 g/g.mol. By reaction with T.B.A.I. (0.2 milliequivalent) and PVL (1.5 g) there are obtained 21.4 g of a polymer having the
20 following composition: PVL: 6.5% by weight - p.vinylbiphenyl: 28% by weight and BUT: 65.5% by weight. The Differential Thermal Analysis exhibits the expected transitions for butadiene (-85°C), for p.vinylbiphenyl (+161°C) and for PVL (+209°C).

EXAMPLE 7

- The previous test is repeated, the only difference being that 2-vinylnaphthalene is employed. A product is obtained which has a composition akin to that of Example 6. The Differential Thermal Analysis
30 (D.T.A.) exhibits the expected transitions, viz.: -85°C (polyBUT) - +151°C (polyvinylnaphthalene) and +205°C (polyPVL).

EXAMPLE 8

- The polymerization step is carried out in THF (tetrahydrofuran) (50 mls) at -78°C:
35 2-isopropenylnaphthalene (10 g) with Li.nor.butyl (0.5 millimol). Then there are added 2 g of butadiene and subsequently, at room temperature, 28 g of butadiene in 300 mls of cyclohexane, carrying out the polymerization at 60°C for about one hour. On completion of this step, functionalization with CO₂ is carried out according to the procedural steps described hereinabove. The -COOH-functionalized polymer
45 (40 g) contains 75% by weight of butadiene having a predominance of the 1-2 structure. Such a polymer is hydrogenated under conventional conditions with a palladium-based (10% Pd) on charcoal. The ¹H NMR test exhibits the complete absence of unsaturations.
50 This product is subsequently employed for grafting the PVL block (2.5 g) according to the procedure with T.B.A.I. (0.25 millimol). There are isolated 42.5 g of a polymer having the following composition: poly - 2 - isopropenylnaphthalene: 23.5% by weight, poly
55 PVL: 6% by weight and C₂-C₄: 70.5% by weight. At the D.T.A. (Differential Thermal Analysis) the expected transitions have been seen at -60°C (C₂-C₄) - +220°C (polyisopropenylnaphthalene) and the melting at +207°C for polyPVL.

EXAMPLE 9

- The procedure is the same as for the previous example, the only difference being that paraisopropenylnaphthalene is used. The processing run is the same and there are isolated 42.5 g of a product, which has the
65 expected composition. The D.T.A. exhibits the transi-

tions at -60°C, +225°C and +209°C, which can be ascribed, respectively, to the C₂-C₄ blocks, to polyisopropenylnaphthalene and polypivalolactone.

CLAIMS

- 70 1. A block copolymer of the pattern A_xB_yC_z in which A_x is an aromatic polyvinyl and/or polyisopropenylnaphthalene sequence, B_y is a diene sequence (optionally hydrogenated), C_z is a polypivalolactone sequence, and x, y, and z are integers which represent the
75 monomeric units in the respective sequences, the transition temperature of the A_x sequence being equal to or higher than 140°C.
2. A block copolymer according to claim 1, wherein the vinyl and/or isopropenylnaphthalene compound of the A_x sequence is selected from
80 aliphatic styrene, vinylbiphenyl, isopropenylnaphthalene, vinylnaphthalene and isopropenylnaphthalene.
3. A block copolymer according to claim 1 or 2,
85 wherein the diene compound of the B_y sequence is selected from 1,3 - butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, 1,3 - pentadiene (piperylene), 2 - methyl - 3 - ethyl - 1,3 - butadiene, 3 - methyl - 1,3 - pentadiene, 1,3 - hexadiene, 2 - methyl - 1,3 - hexadiene and 3 - butyl - 1,3 - octadiene.
4. A block copolymer according to claim 1, 2 or 3, the diene sequence having been hydrogenated.
5. A block copolymer according to claim 1, substantially as herein described.
- 90 6. A process for the preparation of a block copolymer according to claim 1, comprising (a) effecting polymerization of a vinyl and/or isopropenylnaphthalene monomer; (b) effecting addition of a diene to the product formed in step (a); (c) effecting functionalization of the living polymer AB
95 obtained in step (b) with carboxyl groups by initially reacting the living polymer AB with carbon dioxide and subsequently setting free the carboxyl function by an acidic treatment; and (d) effecting addition of
100 pivalolactone to the polymer obtained in step (c).
7. A process according to claim 6, wherein step (a) is effected in the presence of an aliphatic, cycloaliphatic, aromatic, alkyl aromatic, apolar, or aprotic solvent.
- 110 8. A process according to claim 6 or 7, wherein step (a) is carried out in the presence of an initiator selected from alkyls, hydrides and amides of alkali metals.
9. A process according to claim 8, wherein the
115 initiator is Li-sec.butyl.
10. A process according to any of claims 6 to 9, wherein step (a) is carried out at a temperature of from -80°C to 150°C.
11. A process according to claim 10, wherein
120 step (a) is carried out at a temperature of from -30°C to 80°C.
12. A process according to any of claims 6 to 11, wherein step (b) is carried out in the presence of an aliphatic, cycloaliphatic, aromatic, alkyl aromatic or
125 apolar aprotic solvent.
13. A process according to any of claims 6 to 12, wherein step (b) is carried out in the presence of an alkyl, hydride or amide of an alkali metal.
14. A process according to any of claims 6 to 13,
130 wherein step (b) is carried out at a temperature of

from -50°C to 150°C .

15. A process according to claim 14, wherein step (b) is carried out at a temperature of from 0°C to 60°C .

5 16. A process according to any of claims 6 to 15, wherein step (c) is carried with a CO_2 saturated solution.

17. A process according to claim 16, wherein the solvent is selected from aliphatic and/or cycloaliphatic solvents.

10 18. A process according to any of claims 6 to 17, wherein step (c) is carried out at a temperature of from -50°C to 20°C .

19. A process according to claim 18, wherein step (c) is carried out at a temperature of from -5°C to 5°C .

20. A process according to any of claims 6 to 19, wherein, in step (c), the carboxyl function is set free by an acidic treatment.

20 21. A process according to any of claims 6 to 20, wherein step (d) is carried out with a mixture of toluene and tetrahydrofuran.

22. A process according to any of claims 6 to 21, wherein step (d) is carried out in the presence of a
25 tetralkylammonium salt having the general formula:



wherein R^{I} , R^{II} and R^{V} , which are the same or
30 different, are each an alkyl chain containing from 1 to 8 carbon atoms.

23. A process according to claim 6, substantially as described in any of the foregoing Examples.

24. A block copolymer prepared by a process
35 according to any of claims 6 to 23.