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The invention relates to the polymerization of at least one polymerizable or copolymerizable monomer by the radical route in the presence of a stable free radical and of a polymerization initiator.

5 The presence of a stable free radical in a polymerization mixture makes it possible to control the growth of the polymer chains and generally to result in a polymer of low polydispersity, indeed with a polydispersity in the region of unity, as is possible in anionic
10 polymerization. The presence of the stable free radical exhibits, however, the disadvantage of greatly slowing down the reaction rate and of making it difficult, indeed impossible, to obtain polymers with a high weight-average molecular mass, for example greater than 50,000. It is
15 possible to attempt to overcome this disadvantage by adding a polymerization initiator to the polymerization. However, to date, the initiators used in mixtures comprising a polymerizable monomer and a stable free radical cause side reactions reflected by the partial destruction of the stable
20 free radical and of the initiator itself and by the formation of impurities which damage in particular the appearance of the final polymer. Due to these side reactions, the initiator has little effectiveness, lengthening the reaction times and making it difficult to obtain polymers with a high molecular
25 mass. Moreover, the final polymer is coloured and often opaque.

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describes a polymerization process in the presence of a stable free radical and of benzoyl peroxide as polymerization initiator. The polymers thus obtained have a number-average molecular mass of less than 60,000 and a weight-average molecular mass of less than 70,000 and moreover have a high yellowing index.

US Patent 4,581,429 describes a polymerization process which confers control on the formation of the growing polymer chains. This process requires the preparation of an alkoxyamine and results in oligomers with a molecular mass of less than 10,000. This process exhibits low rates of conversion of monomer to polymer.

The following references may also be of interest:
WO 95/26987, US 5,412,047, US 5,449,724 and BR 9400671.

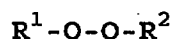
In these prior art documents, the polymerization initiator is never regarded as being an essential factor of the process described.

It has now been found that the use of a specific family of polymerization initiators makes it possible to overcome the abovementioned disadvantages. The process according to the invention is fast, allows the initiator to act more effectively and results in polymers or copolymers having a low yellowing index according to ASTM standard D 1925.

According to one aspect of the present invention, there is provided a process for the manufacture of a polymer or copolymer which process comprises polymerizing or



copolymerizing at least one polymerizable or copolymerizable monomer by the radical route in the presence of a stable free radical and of an initiator of formula



- 5 in which each of R^1 and R^2 , which may be the same or different, represents an alkyl, aryl, alkylaryl or aralkyl radical comprising, for example, up to 20 carbon atoms.

Preferably, at least one of the radicals R^1 and R^2 comprises an aromatic ring. The initiator used preferably has
10 a half-life of one hour at a temperature between 80°C and 150°C and more preferably at a temperature between 100°C and 130°C.

Mention may be made, by way of example of initiators, of:

- 15 - di-tert-butyl peroxide,
 - tert-butyl cumyl peroxide,
 - dicumyl peroxide.

Dicumyl peroxide is a particularly suitable initiator.

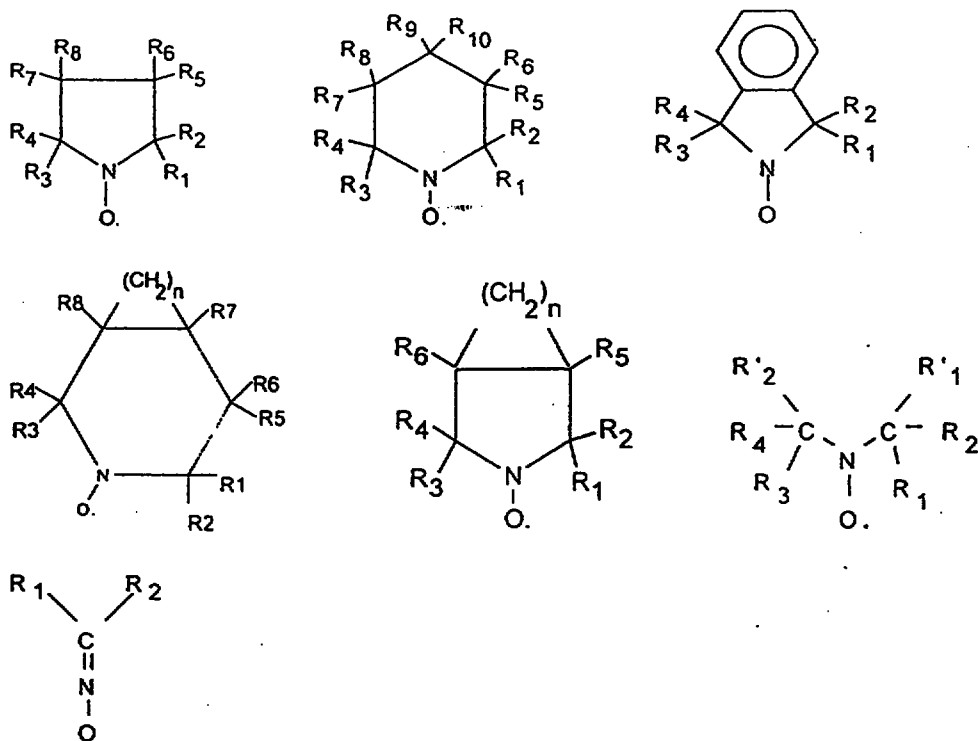
- 20 The initiator can be introduced into the polymerization or copolymerization mixture in an amount of 50 to 50,000 ppm by weight, based on the mass of polymerizable or copolymerizable monomer.

A stable free radical should not be confused with
25 free radicals with a fleeting lifetime (a few milliseconds), such as the free radicals resulting from the usual polymerization initiators such as peroxides, hydroperoxides



and initiators of azo type. Free radicals which are polymerization initiators tend to accelerate the polymerization. In contrast, stable free radicals generally tend to slow down the polymerization. It may be generally
5 said that a free radical is stable within the meaning of the present invention if it is not a polymerization initiator and if, under the conditions of use of the present invention, the mean lifetime of the radical is at least five minutes. During this mean lifetime, the molecules of the stable free radical
10 continually alternate between the radical state and the state of a group bonded via a covalent bond to a polymer chain. Of course, it is preferable for the stable free radical to exhibit good stability throughout the duration of its use in the context of the present invention. Generally, a stable
15 free radical can be isolated in the radical state at room temperature.

The family of the stable free radicals includes compounds acting as radical polymerization inhibitors, stable nitroxide radicals, that is to say comprising the $=N-O^{\bullet}$
20 group, such as the radicals represented by the following formulae:



in which each of R₁, R₂, R₃, R₄, R'₁ and R'₂, which may be the same or different, represents a halogen atom, such as chlorine, bromine or iodine, a saturated or unsaturated, linear, branched or cyclic hydrocarbon group, such as an alkyl or phenyl group, or an ester group -COOR or an alkoxy group -OR, or a phosphonate group -PO(OR)₂, or a polymer chain which can be, for example, a poly(methyl methacrylate) chain, a polybutadiene chain or a polyolefin chain, such as a polyethylene or polypropylene chain, but which is preferably

a polystyrene chain, and each of R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} , which may be the same or different, can be chosen from the same family of groups as for R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , and can furthermore represent a hydrogen atom, a hydroxyl group -
5 OH, or an acid group such as $-COOH$ or $-PO(OH)_2$ or $-SO_3H$.

In particular, the stable free radical can be 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, sold under the trade name Proxyl, or 2,2,6,6-tetramethyl-1-piperidinyloxy,
10 generally sold under the name Tempo.

The stable free radical can also be chosen from the following list:

- tert-butyl 1-phenyl-2-methylpropyl nitroxide,
- tert-butyl 1-(2-naphtyl)-2-methylpropyl
15 nitroxide,
- tert-butyl 1-diethylphosphono-2,2-dimethyl propyl nitroxide,
- tert-butyl 1-dibenzylphosphono-2,2-dimethyl-propyl nitroxide,
- 20 - phenyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide,
- phenyl 1-diethylphosphono-1-methylethyl nitroxide,
- 1-phenyl-2-methylpropyl 1-diethylphosphono-1-methylethyl nitroxide.

25 The stable free radical can be introduced into the polymerization or copolymerization mixture in an amount of 0.005% to 5% by weight, based on the sum of the mass of

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polymerizable monomer and of stable free radical.

The molar ratio of the stable free radical to the initiator is preferably between 1.5 and 2.5, more preferably in the region of 2.

5 A monomer exhibiting a carbon-carbon double bond capable of polymerizing or copolymerizing by the radical route can be used.

At least one monomer present in the polymerization or copolymerization mixture can be a vinylaromatic monomer or an
10 olefin or a diene or an acrylic or methacrylic monomer. The monomer can also be vinylidene difluoride or vinyl chloride.

Vinylaromatic monomer is understood to mean styrene, styrene substituted (e.g. on the vinyl group) by an alkyl group, for example α -methylstyrene or ortho-vinyltoluene,
15 para-vinyltoluene, ortho-ethylstyrene or 2,4-dimethylstyrene, or styrene substituted on the ring by halogen, for example, 2,4-dichlorostyrene, as well as vinylanthracene, chloromethylstyrene or para-acetoxystyrene.

Diene is understood to mean in particular a conjugated
20 diene comprising from 4 to 8 carbon atoms, for example 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene or chloroprene.

The process according to the invention is more particularly effective in the case of vinylaromatic monomers
25 and of dienes.

Apart from the distinctive characteristics of the present invention as regards the initiator and the stable

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free radical, the polymerization or copolymerization is carried out under the usual conditions known to the person skilled in the art, taking into account the monomer or monomers used and that the polymerization or copolymerization
5 takes place by a radical mechanism.

When the mixture comprises a vinylaromatic monomer and excellent control of the growth of the polymer or copolymer is desired, so that the latter has a particularly narrow polydispersity, it is preferable to carry out the
10 polymerization or copolymerization at a temperature at which no polymerization or copolymerization is observed in the absence of the initiator. For example, in the case of the polymerization or copolymerization of at least one vinylaromatic monomer, this situation exists when the
15 temperature is less than approximately 120°C. Appreciable polymerization or copolymerization rates are nevertheless obtained by the process of the invention when the temperature is between 90°C and 120°C.

Nevertheless, if higher polydispersity is acceptable,
20 the mixture can be heated at higher temperatures.

Thus, when the mixture comprises a vinylaromatic monomer, it is possible to carry out the polymerization or copolymerization at between 50°C and 120°C but it is also possible to heat to 200°C, if a greater rate of
25 polymerization is preferred to the detriment of the polydispersity.

The process according to the invention can be carried

out at 50 to 200°C and preferably at 100 to 130°C.

When an impact vinylaromatic polymer is to be obtained, the polymerization or copolymerization mixture generally comprises at least one vinylaromatic monomer and a
5 rubber, the latter generally being conjugated polydiene, such as one or more polybutadienes.

The invention also relates to the preparation of copolymers. For example, when at least one vinylaromatic monomer is present in the mixture, this monomer can be
10 copolymerized with, for example, at least one monomer chosen from acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, an alkyl ester in which the alkyl group contains from 1 to 4 carbon atoms, an N-alkylmaleimide in which the alkyl group contains from 1 to 4 carbon atoms, and
15 N-phenylmaleimide.

The process according to the invention makes possible the preparation of block copolymers. Indeed, the polymerization of a first monomer in the presence of a stable free radical results in a living polymer block. It is then
20 possible to attach, to this first block, a block of another polymer, the first living polymer block being placed in a mixture for the polymerization of a second monomer. It is thus possible to produce block copolymers, for example copolymers comprising one or more polystyrene blocks and one
25 or more polybutadiene blocks. The preparation of such copolymers by the radical route requires good control of the polymerization of each of the blocks. Indeed, if a

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termination reaction interrupts the growth by polymerization of a block, it will not be possible to attach a block of another monomer to it. The termination reactions must thus be as infrequent as possible. There are fewer termination
5 reactions when, during the polymerization, the number-average molecular mass is more closely linearly proportional to the percentage of conversion. The existence of termination reactions is reflected by a decrease in the rate of increase in the number-average molecular mass as a function of the
10 percentage of conversion.

The process according to the invention is particularly suited to polymerization or copolymerization in the organic phase, in the absence of aqueous phase, as is the case in bulk processes or solution processes in an organic solvent. -

15 Of course, depending on the polymerization or copolymerization conditions, and in particular the duration, the temperature and the degree of conversion of monomer to polymer or copolymer, it is possible to prepare products of very different molecular mass.

20 The invention relates both to the preparation of oligomers, polymers or copolymers with a weight-average molecular mass of less than 10,000 and to the preparation of polymers or copolymers with a weight-average molecular mass of greater than 10,000, such as high polymers with a weight-
25 average molecular mass generally ranging from 100,000 to 400,000.

The invention relates both to polymerization or



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copolymerization processes in which the degree of conversion of monomer to polymer or copolymer is less than 50% and to those in which the degree of conversion of monomer to polymer or copolymer is greater than 50%. For example, the degree of
5 conversion of monomer to polymer or copolymer can exceed 60% and generally ranges from 65% to 80%.

The process according to the invention results in a polymer or copolymer (which includes oligomers) with a polydispersity generally of less than 1.9 and with a
10 yellowing index, measured according to ASTM standard D 1925, generally of less than 20, indeed 10 and even 5.

When the molar ratio of the amount of stable free radical to the amount of monomer is greater than 1.2, the polydispersity of the final polymer or copolymer is generally
15 less than 1.5.

According to a further aspect, the invention provides a polymer or copolymer with a polydispersity of less than 1.9, preferably less than 1.5, and with a yellowing index of less than 20, preferably less than 10, and more preferably
20 less than 5. Suitably such a polymer or copolymer is a polymer or copolymer of at least one vinylaromatic monomer.

The invention is further illustrated in the following Examples.

The following characteristics were used in the
25 Examples:

- % of conversion: % of monomer converted to polymer. It was determined by ^1H NMR on a Bruker 200 MHz device with

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integration of the peaks corresponding to the polymer and to the monomer.

- Number-average molecular mass (represented by M_n): gel permeation chromatography in THF at 30°C, after calibration with standard polystyrene samples.

- Polydispersity index (represented by PI): ratio of the weight-average molecular mass to the number-average molecular mass, both measured by GPC (see M_n above).

- Efficiency: the "efficiency" is equal to the ratio of the theoretical number-average molecular mass to the experimental number-average molecular mass. The theoretical number-average molecular mass is given by the formula:

$$M_{n\ th} = \frac{(M)_s - (M)}{2[(I)_s - (I)]}$$

in which (M) , $(M)_s$, (I) and $(I)_s$ respectively represent the molar concentrations (in mol per litre) of monomer, starting monomer, initiator and starting initiator.

The concentration (I) as a function of the time (t) is determined by the equation:

$$(I) = (I)_s e^{-K_d t}$$

in which K_d represents the rate constant for decomposition of the initiator at the temperature under consideration.

The closer the efficiency approaches the value of 1,

the more effective the initiator and the stable free radical in controlling the polymerization and the less they participate in the undesirable side reactions which partly destroy them.

5 **EXAMPLES 1 to 7**

A 100-ml two-necked reactor equipped with a stirrer system and with a temperature control is purged by vacuum/nitrogen cycles and then the following are introduced into the reactor under nitrogen and at room temperature:

- 10 - 50 g of styrene (0.481 mol), then
- an amount of initiator such that the molar ratio of the initiator to the styrene is equal to $C_{\text{initiator}}$, the value of which is shown at the top of Tables 1 to 7 (C_{Dicum} when the initiator used is dicumyl peroxide and C_{Benz} when the
- 15 initiator used is benzoyl peroxide).

 - an amount of 2,2,6,6-tetramethylpiperidinyloxy (commonly known as Tempo), such that the molar ratio of the Tempo to the initiator is 2.

The reactor is then brought to 125°C with stirring

20 until the reaction mixture sets solid. The moment at which the mixture reaches the temperature of 125°C is defined as being the starting moment of the test.

The polymer is then cooled to room temperature and then dissolved in 10 times its weight of tetrahydrofuran

25 (THF). The polymer is then precipitated by pouring the solution in THF obtained dropwise in 10 times its volume of methanol. The polystyrene collected is analysed by gel

permeation chromatography (GPC). The results are combined in Tables 1 to 7.

These results show the change in the formation of the polymer as a function of the time.

5 **EXAMPLE 8**

After purging by vacuum/nitrogen cycles, 300 g of styrene, 4.5 millimol of dicumyl peroxide and 15 millimol of stable free radical Tempo are introduced, at 20°C and under nitrogen, into a 1-litre glass reactor equipped with an anchor stirrer and with a temperature control. The combined mixture is brought to 125°C. The moment at which the mixture reaches the temperature of 125°C is defined as being the starting moment of the test. Samples are withdrawn over the course of time for analysis. The results relating to the monitoring of the formation of the polymer over the course of time are combined in Table 8.

The polymer obtained after polymerizing for 5 hours and 30 min is then degassed in an oven under a vacuum with a residual pressure of 25 mbar for 20 minutes at 200°C: it is then shaped into a slab with a thickness of 3 mm in a press for 10 minutes, comprising preheating for 5 minutes from room temperature to 170°C and then pressing for 5 minutes at 170°C under 200 bars. The yellowing index is then measured on the slab, according to ASTM standard D 1925. The yellowing index is 2.

EXAMPLE 9 (comparative)

The reaction is carried out as in Example 8, except

that dicumyl peroxide is replaced by the same amount of benzoyl peroxide. The results relating to the monitoring of the formation of the polymer over the course of time are combined in Table 9. The yellowing index in this instance is 34.9.

EXAMPLE 1; $C_{\text{DICUM}} = 0.02$				
Time (h)	% conversion	Mn measured	PI	Efficiency
1	2	300	1.05	
5	4	300	1.05	
10	5	300	1.05	
12	5	300	1.05	
15	7	300	1.05	
16	10	300	1.05	
17	25	650	1.07	
18	35	700	1.09	1.1
19	45	960	1.12	1.1
20	50	1050	1.12	1.1
21	55	1100	1.13	
22	60	1200	1.13	1.1
23.75	60	1300	1.14	1
26	60	1400	1.15	1

TABLE 1

EXAMPLE 2 (COMPARATIVE); $C_{\text{BENZ}} = 0.02$				
Time (h)	% conversion	Mn measured	PI	Efficiency
3.5	7.4	-	-	
5	8	-	-	
9	9	-	-	
14	12.5	-	-	
18	16.4	560	1.11	
22	20	-	-	
27	28	1500	1.11	0.5
32	32	-		
38	37	1750	1.15	0.5
44	42	2200	1.16	0.5
51	45	2200	-	
58	47	2200	1.22	0.5
65	49	2200	1.32	0.5
74	50	2200	1.32	0.6

TABLE 2

EXAMPLE 3; $C_{DICUM} = 0.01$				
Time (h)	% conversion	Mn measured	PI	Efficiency
1	2	300	1.00	
3	2.5	300	1.00	
5	3	300	1.00	
7	4	300	1.00	
9	6	300	1.00	
10	8	300	1.00	
11	9	300	1.00	
12	10	300	1.00	
13	11	300	1.00	
14	12	300	1.00	
15	13	300	1.00	
16	15	450	1.05	
17	50	2200	1.3	1.1
18	78	3600	1.26	1.1
18.5	90.5	4200	1.23	1.1

TABLE 3

EXAMPLE 4 (COMPARATIVE); $C_{\text{BENZ}} = 0.01$				
Time (h)	% conversion	Mn measured	PI	Efficiency
3.5	3	-	-	
5	5	-	-	
11	12	450	1.07	
21	24	2200	1.14	0.6
24	31	2600	1.16	0.6
28	37	2700	1.27	0.7
31	43	3100	1.22	
34	44	3350	1.15	0.7
37	47	3600	1.20	0.7
42	57	4200	1.20	0.7
47	63		-	
51	67	4300	1.23	0.8
55	78	4650	1.23	0.9
61	90	5000	1.23	1

TABLE 4

EXAMPLE 5; $C_{DICUM} = 0.00125$				
Time (h)	% conversion	Mn measured	PI	Efficiency
4	1.5	300	1.00	
6	2.5	300	1.00	
10	38	12,600	1.4	
11	54	16,700	1.4	
11.75	68	21,800	1.4	
13	81	29,000	1.34	1.1

TABLE 5

EXAMPLE 6; $C_{DICUM} = 0.0005$				
Time (h)	% conversion	Mn measured	PI	Efficiency
3	1.5	300		
4	2	300		
5	7.5	11,000	1.7	0.7
6	22	21,200	1.71	1
7	31	30,000	1.63	1
8	41	39,400	1.57	1
9	50.8	47,000	1.54	1
10	60	54,000	1.56	1.1
11	71	66,000	1.53	1.1

TABLE 6

EXAMPLE 7; $C_{\text{Dicum}} = 0.000166$			
Time (h)	% conversion	Mn measured	PI
1	1	300	
3	9	33,600	1.8
4	25	66,000	1.6
5	40	76,600	1.6
6.5	63	104,000	1.6

TABLE 7

EXAMPLE 8; $C_{\text{Dicum}} = 0.0026$			
Time (h)	% conversion	Mn measured	PI
1	0.2		
4	52.6	10,600	1.4
5	71.2	14,170	1.3
5.5	85	15,400	1.3

TABLE 8

5

EXAMPLE 9 (Comparative); $C_{\text{Benz}} = 0.0026$			
Time (h)	% conversion	Mn measured	PI
1	1.2		
4			
5	22.6		
5.5	28	6141	1.2
8.5	49.9	10,950	1.3
11	63	13,320	1.3

TABLE 9



CLAIMS

1. Process for the manufacture of a polymer or copolymer which process comprises polymerizing or copolymerizing by the radical route of at least one monomer
5 in the presence of a stable free radical and of an initiator of formula



in which each of R^1 and R^2 , which may be the same or different, represents an alkyl, aryl, alkylaryl or aralkyl
10 radical.

2. Process according to Claim 1, in which at least one of the radicals R^1 and R^2 comprises an aromatic ring.

3. Process according to Claim 2, in which the
15 initiator is dicumyl peroxide.

4. Process according to any one of Claims 1 to 3, in which the initiator is introduced into the polymerization or copolymerization mixture in an amount of 50 to 50,000 ppm by weight, based on the mass of monomer.

20 5. Process according to any one of Claims 1 to 4, in which the stable free radical is introduced in an amount of 0.005 to 5% by weight based on the sum of the mass of monomer and of stable free radical.

6. Process according to any one of Claims 1 to 5,
25 in which the molar ratio of the stable free radical to the initiator is from 1.5 and 2.5.

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7. Process according to any one of Claims 1 to 6, in which the molar ratio of the amount of stable free radical to the amount of monomer is greater than 1.2.
8. Process according to any one of Claims 1 to 7, in which at least one monomer is vinyl-aromatic.
9. Process according to any one of Claims 1 to 7, in which at least one monomer is a diene.
10. Process according to any one of Claims 1 to 9, in which the polymerization or copolymerization temperature is 100°C to 130°C.
11. Process according to any one of Claims 1 to 10, in which the polymerization or copolymerization is carried out in the organic phase, in the absence of aqueous phase.
12. Process according to any one of Claims 1 to 11, in which the degree of conversion of monomer to polymer is greater than 50%.
13. Process according to Claim 12, in which the degree of conversion is greater than 60%.
14. Process according to Claim 12, in which the degree of conversion is from 65 to 80%.
15. A polymer or copolymer obtained by the process claimed in any one of claims 1 to 14.
16. Polymer or copolymer with a polydispersity of less than 1.9 and with a yellowing index, measured according to ASTM standard D 1925, of less than 20.
17. Polymer or copolymer according to Claim 16,

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which has a yellowing index of less than 10.

18. Polymer or copolymer according to Claim 16, which has a yellowing index of less than 5.

19. Polymer or copolymer according to any one of 5 Claims 16 to 18, which has a polydispersity of less than 1.5.

20. Polymer or copolymer according to any one of Claims 16 to 19, which is a polymer or copolymer of at least one vinylaromatic monomer.

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