

Hydroxytelechelic Hydrocarbon Copolymers with High Aging Resistance for Elastomeric Materials

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Received 21 December 2009; accepted 26 March 2010

DOI 10.1002/app.32535

Published online 7 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dihydroxytelechelic copolyalkenamers were prepared via metathetical polymerization of cyclic olefins (cyclooctadiene, cyclooctene and cyclododecene) in presence of first generation Grubbs catalyst and butene diacetate as functionalizing chain transfer agent in order to study their aging resistance. The influence of compositions and molar masses of the copolyalkenamers were investigated in terms of thermo-mechanical properties. Increasing chains length or the proportion of polycyclooctadiene allow to get non-crystalline polymers. Low T_g materials (between -78°C and -108°C) were prepared. The resistance towards oxidation of the different copolyal-

kenamers was carried out using a viscosity measurement method. A critical time, corresponding to a brutal increase of the apparent viscosity, was related to degradation of the polymers and was shown to be dependent on the Csp^2 proportion in the structure. The absence of vinylic units and the decrease of the double bonds content within the copolymers were proved to enhance the stability of the copolyalkenamers towards aging resistance. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1830–1836, 2010

Key words: polyalkenamers; hydroxytelechelic; aging resistance; low glass transition temperature

INTRODUCTION

Hydroxytelechelic polybutadiene (HTPB), with one or more hydroxyl end groups, are used in a lot of industrial applications as precursors of elastomeric materials¹ like polyurethanes or polyesters. HTPB hydrocarbon backbone give them excellent elastomeric properties until very low temperatures, as their T_g are as low as -70°C . Because the HTPB chains have a lot of unsaturations, they are very sensitive to oxidative phenomena giving recombination reactions leading to intermolecular crosslinking of the chains^{2–13} yielding a very fast aging of the material and the loss of the elastomeric properties. Polydienes aging studies^{14–17} showed that vinylic unsaturations played a predominant role in the aging process and the 1,4 units had a better resistance to this phenomenon. However, the latter are not totally inert and they also let to radical crosslinking reactions, induced by double bond photo oxidation, with slower kinetics.

Commercially produced HTPB obtained by radical polymerization of 1,3-butadiene in the presence of hydrogen peroxide^{18–20} contains both 1,2 and 1,4 units (respectively about 25 and 75%), with primary, secondary, and tertiary hydroxyl end groups coming from some recombination termination and grafting due to a strong reactivity of the initiator and transfer

reactions²¹ to usual alcoholic solvents. The ease of the HTPB preparation by radical polymerization is balanced by the lack of regiospecificity as well as end group specificity. Living anionic polymerization therefore offers a potential solution^{22–24} but remains limited due to still some percents of 1,2 units, costly purity cares, and a necessary termination with an oxirane. Ring Opening Metathesis Polymerization (ROMP) of cyclic olefins of various sizes gives opportunity to get rid of vinylic units^{25,26} and to decrease the number of backbone unsaturations. Polycyclooctene revealed an improved stability but at the same time exhibit some limiting crystallinity due to interactions between methylene groups in the number of six per repetitive units.^{27,28}

In this article, we show that hydroxytelechelic copolyalkenamers synthesized by ROMP using a metal alkylidene catalyst and a chain-transfer agent can have a better aging resistance than hydroxytelechelic polybutadienes. The suppression of vinylic unsaturations followed by a reduction of the global unsaturations rate as well as the composition of the copolymers are investigated to improve the aging resistance of these hydrocarbon precursors and corresponding elastomeric materials.

EXPERIMENTAL

Materials

1,5-Cyclooctadiene (COD) (99%, Aldrich), *cis*-cyclooctene (COE) (95%, Aldrich), cyclododecene (CDD)

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(*cis/trans* mixture, 96%, Aldrich), *cis*-1,4-diacetoxy-2-butene (butene diacetate) (95%, Aldrich) and dichloromethane (99%, J.T. Baker) were purified over CaH₂, distilled under vacuum and used without storage. The Grubbs catalyst of first generation (C₄₃H₇₂Cl₂P₂Ru) (Aldrich) was used without any purification.

Procedures

All polymerizations and copolymerizations were performed at room temperature for several hours under vacuum in a glass reactor previously flamed under vacuum equipped with a magnetic stirrer and fitted with PTFE stopcocks. Monomer(s), transfer agent (butene diacetate) and catalyst were introduced in the reactor via a glove box under argon. Dichloromethane was then added under vacuum through a connected glass tube. The mixture was precipitated in an acidic solution of methanol (HCl/MeOH 1/10) and the copolymer washed with the acidic solution of methanol followed by pure methanol. The copolymer was finally dried under vacuum.

Typically, in a 50 mL glass reactor equipped with a magnetic stirrer previously flamed under vacuum, 5.5 mL of COE (4.1×10^{-2} mol), 7.9 mL of CDD (4.1×10^{-2} mol), and 0.03 mL of butene diacetate (1.9×10^{-4} mol) were introduced, via a glove box under argon, followed by 7 mg of the Grubbs complex (8.5×10^{-6} mol). Five milliliter of dichloromethane was then added under vacuum through a connected glass tube and the reaction was let stirred at room temperature for 2.5 h. After that time the 50/50 expected copolymer *p*(COD-*co*-COE) was precipitated in an acidic solution of methanol, washed with the same solution followed with pure methanol, and finally dried under vacuum. The absence of residual monomer was checked by gas chromatography and monomers ratio by ¹H-NMR. Experimental and theoretical ratios were matching quite well for all copolymers (experimental $\overline{M}_n = 28,900$ g/mol, $I_p = 1.8$, $T_g = -81^\circ\text{C}$).

Deprotection of hydroxyl groups^{25,29,30}. Acetate groups were hydrolyzed in basic condition by addition of sodium methoxide in methanol to the polymer dissolved in THF. The mixture was stirred 2 h at room temperature then precipitated in an acidic methanolic solution (HCl/MeOH 1/10). The polymer was finally washed three times with methanol.

Polyalkenamers functionality (\overline{F}_n) was checked by ¹H-NMR. A polycyclooctadiene ($\overline{M}_n = 8\,700$ g/mol, UV detection) is chosen as example: =CH(1)–CH₂(2)–CH₂(3)–CH(4)=: 2 and 3 at 2.0–2.2 ppm; 1 and 4 at 5.3–5.7 ppm. Chain ends are as follow: –CH(a)=CH(b)–CH₂(c)–OH: *a* and *b* at 5.65 ppm; *c* at 4.1–4.2 ppm. Calculated $\overline{DP}_n = 161$ (approximation due to PS standards used). \overline{F}_n can be given by

the integration ratio between 5.3–5.7 ppm and 4.1–4.2 ppm. For all hydroxytelechelic polymers functionality close to 2 was calculated.

Instrumentation

Polyalkenamers molar masses were determined by SEC at 20°C using THF as eluant on a Jasco apparatus equipped with a Varian 2510 HPLC-pump, a refractive index/UV detectors and fitted with four TSK gels HXL columns (2000, 3000, 4000, and 5000) at an elution rate of 0.8 mL/min with polystyrene as standards.

The glass transition temperatures and crystallinity properties of polyalkenamers were determined by Differential Scanning Calorimetry (DSC) on a Perkin-Elmer DSC7.

The apparent viscosity measurements, corresponding to the ratio of shear stress to shear rate, were carried out by increasing shear rate from 0.1 to 500 s⁻¹ with a ThermoHaake Rheostress 300 rheometer. The polymer (0.5 mL) was placed on the fixed plate of the rheometer and a gap of 1 mm between the plate and the flat mobile was chosen. The Newtonian plateau of the polymer was first determined between 60 and 100°C by measuring growing values of the shear speed, at which the viscosity is constant. A constant shear speed of the mobile was then selected in the range fitting with the Newtonian plateau and viscosities were recorded with time. Measurements reproducibility was obtained by controlling results for different samples of the same composition. It was checked that the stationary state was reached by comparing viscosities obtained during the shear rate ramp to some values measured by applying a constant shear rate and analyzing the evolution of viscosity with time. The experiment was stopped after the brutal rise of the polymer viscosity, which corresponds to a critical time (t_{critical}) related to the occurrence of crosslinkage within the polyalkenamer.

RESULTS AND DISCUSSION

When polybutadienes or polyalkenamers are subjected to an aging process, which can be accelerated by using high temperatures (up to 100°C), a slow increase of the sample viscosity is observed according to the time.^{31–33} This slow increase was followed by a rapid rise characteristic of the beginning of the gelation, which is the main degradation process.^{27,28} We have chosen the time when this rise starts as a parameter indicating the rate of the polymer aging. This parameter (t_{critical}) has been used as the kinetic measurement of the oxidative aging of the polybutadienes, polyalkenamers, and copolyalkenamers we have prepared. Aging tests at 60 and 100°C under

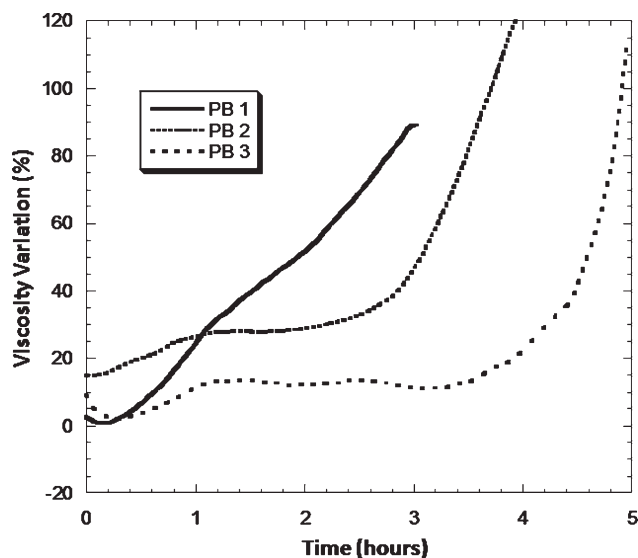


Figure 1 Apparent viscosity variations at 60°C of polybutadiene having different microstructures (1,2 units percentage: PB1 = 62%, PB2 = 25%, PB3 = 1%).

air were carried out at first with different polybutadienes. Similar experiments were done on the same samples in anaerobic conditions, under nitrogen, and have shown a shift of the gelation at higher time with an identical order which depends directly on the nature of polymers. High temperature (60°C) and aerobic medium selected for an optimal window of aging rate of polybutadienes permitted to compare different microstructures and showing the strong implication of the 1,2 units in the crosslinking process (Figs. 1 and 2). The profiles of the apparent viscosity variations were very similar whatever the microstructure with a very rapid increase of the viscosity for a polybutadiene with a ratio of 1,2-units equal to 62% (PB1) and a critical time of crosslinking around 30 min. An increase of the gelation time was observed with a decrease of the vinylic contents. An approximate limit value of about 3 h 40 min for 1% of 1,2 units at 60°C was finally measured.

These results confirmed the predominant role of the 1,2 reactive double bonds in the crosslinking process and also validated this method for the eval-

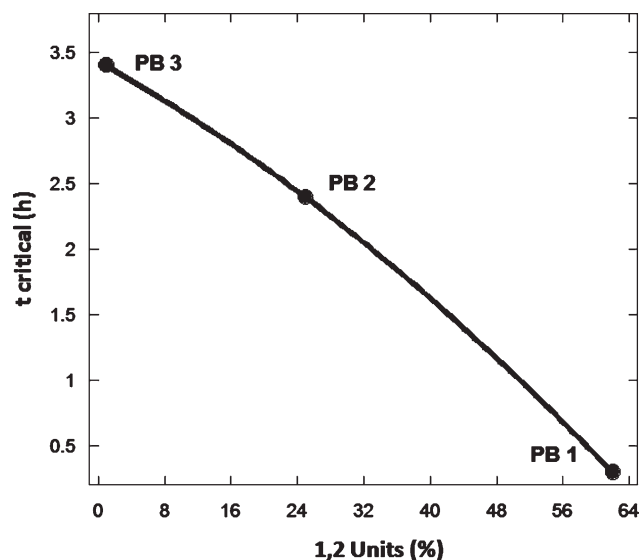


Figure 2 Critical time for crosslinking at 60°C of polybutadienes with microstructures (1,2 units percentage: PB1 = 62%, PB2 = 25%, PB3 = 1%).

uation and comparison of the aging rates of various polydienes. They also allowed to point out the concomitant participation of 1,4 units to the aging of the polymer.

The next step was to decrease the amount of double bonds in the material trying to keep as low as -70°C the glass transition temperature. At first a polybutadiene with 100% 1,4 units content was synthesized by conventional ROMP of 1,5-cyclooctadiene (COD).^{25,26,29,34,35} The hydroxyl groups were introduced with an unsaturated protected diol acting as a chain transfer agent (CTA), which is also responsible for the regulation of the polymers molar mass prepared by ROMP.^{34,36} A functionality close to 2 was calculated by $^1\text{H-NMR}$ for all samples. The decrease of the amount of double bonds on the polymer chains was obtained by ROMP of cycloalkenes having only one double bond for 8 (cyclooctene, COE) or 12 carbons (cyclododecene, CDD). These polyalkenamers were prepared with similar experimental conditions than hydroxytelechelic polyoctadienamer, from cycloolefins in presence of CTA and

TABLE I
Synthesis and Characteristics of Various Polyalkenamers (in dichloromethane at 25°C for 24 h, $[\text{Ru}]/[\text{olefin}] = 10^{-4}$)

Polyalkenamer	% Csp ² ^a (%)	[M] (mol/L)	[M]/[CTA] ^b	Yield (%)	\bar{M}_n th (g/mol)	\bar{M}_n exp (g/mol)	T_g Ip (°C)	Cristallinity ^c (%)	Trans rate ^d (%)	T_m (°C)	Aspect
pCOD	50	2.3	44	>90	4750	5000	1.8 -95	0	68	-	Viscous liquid
pCOE	25	2.7	40	98	4400	4900	1.7 -90	16	54	43	Solid
pCDD	16.8	5.0 ^e	18	85	3000	3400	2.0 -53	35	51	75	Solid

^a Csp² percentage = $n_{\text{Csp}^2}/n \times 100$.

^b [monomer]/[butene diacetate].

^c Measured by DSC.

^d Determined by $^{13}\text{C-NMR}$.

^e Bulk polymerization.

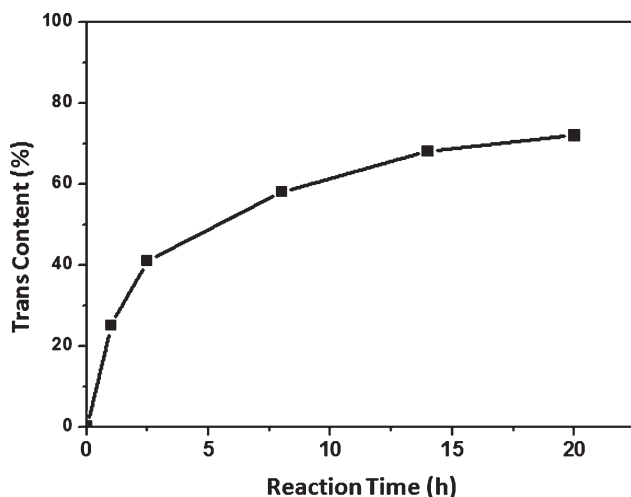


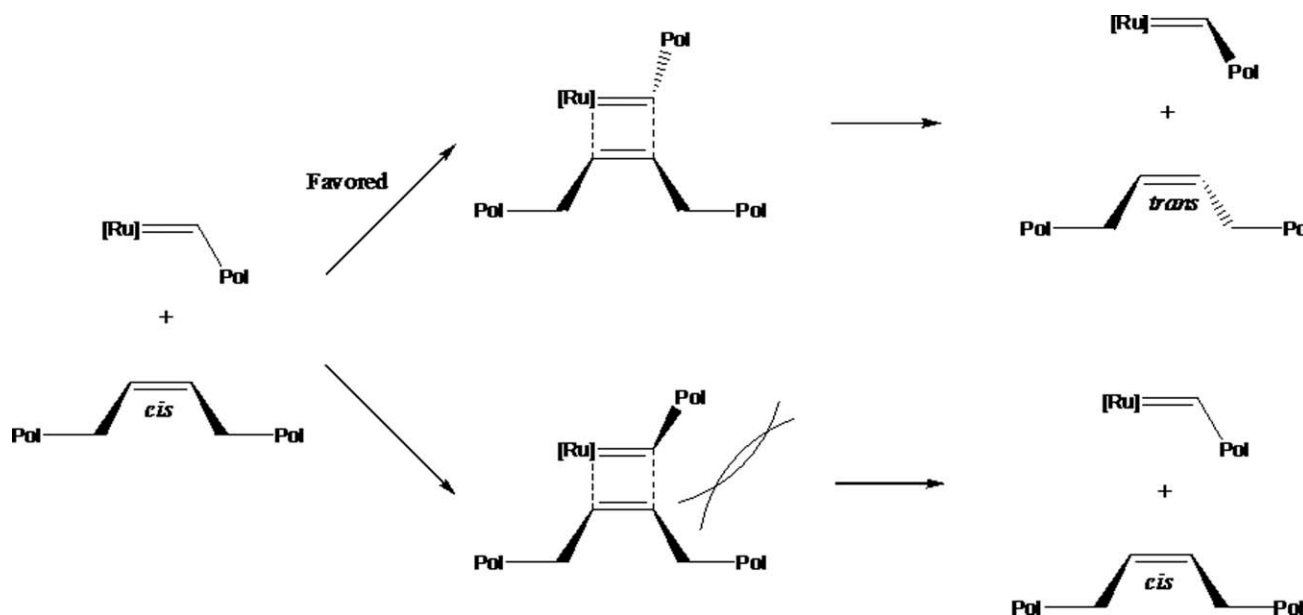
Figure 3 Evolution of the *trans*-content with reaction time during COD ROMP. (20°C, [COD] = 2.3 mol L⁻¹ [catalyst]/[olefins] = 10⁻⁴).

ruthenium vinylalkylidene complex. The ROMP of cyclooctadiene let theoretically to polyoctadienamer (pCOD) having 4 sp² carbons per unit of 8 carbons, representing 50% of sp² carbons. The polyoctenamer (pCOE) contains 2 sp² carbons per unit of 8 carbons corresponding to 25% of sp² carbons and the polydodecenamer (pCDD), with 2 sp² carbons per unit of 12 carbons, contains 16.77% of sp² carbons. As shown in Table I, and as expected, the decrease of the unsaturations rate let to a decrease of the polymer T_g . It is also accompanied by the apparition of melting points related to more regularity of the chains of the materials, due to increasing sp³ carbons content, and a change of state from viscous liquid to solid at room temperature. In addition, and for the

polymerization of cyclooctadiene as example, the proportion of *trans* double bonds increases with reaction time as shown in Figure 3.^{37,38} This is attributed to cross metathesis reactions occurring between two polymer chains. During such redistribution reactions a *cis/trans* double bonds isomerisation takes place, which leads to the preferential formation of *trans* unsaturations because of steric hindrance (Scheme 1). At the isomerization equilibrium, the *trans* content was measured to be around 70% in the case of polyalkenamers synthesized using Grubb's first generation catalyst.

These polymers were then aged by the thermo-oxidative process followed by the viscosity evolution at 100°C (Fig. 4). The measurement of the critical time of crosslinking of polycyclooctadiene (pCOD), the 100% 1,4 units polybutadiene, reveals a higher and better time value than PB2, which corresponds to a high content of 1,2 units (25%), and as expected a similar one with PB3 (1% of 1,2-units). Decreasing the percentage of sp² carbons increases strongly the critical time up to almost 7 h at 100°C for the polycyclododecene (pCDD), as compared with the $t_{\text{critical}} = 3\text{h}20\text{ min}$ for pCOD.

Despite such an aging improvement, the use of pCOE and pCDD can be problematic due to a moderate T_g and their cristallinity. To get over these limitations, random copolymers were synthesized by ROMP of two different cycloolefins. Some results concerning six copolymers constituted by two monomers over three (COD, COE, and CDD) with two different compositions (50–50 and 25–75%) are presented in Table II and Figure 5. Relative high molar masses were chosen to minimize the effect of chain ends toward T_g values. To prevent usual



Scheme 1 Preferential *trans* double bond formation via cross metathesis reaction isomerisation

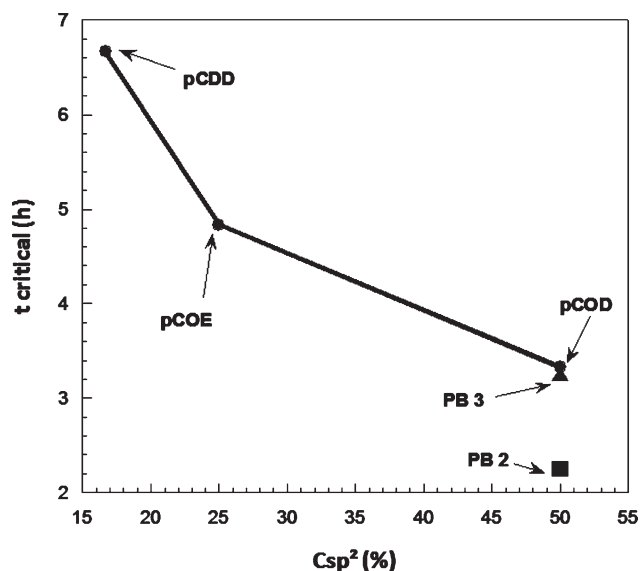


Figure 4 Critical time at 100°C function to 1,4-unsaturations proportion in the polymers.

redistribution reactions and avoid low molar masses polymers, short reactions times or no chain transfer agent were used. Residual monomers were removed by several precipitations in methanol and a drying process. This approach allows the synthesis of copolyalkenamers having various and relatively low unsaturations rate. The DSC measurements show that the copolymers T_g are lower than -78°C and lower than those of the homopolymers. For comparison a 100% 1,4-polybutadiene with 50% of sp^2 carbons, also called polycyclooctadiene, has a T_g equal to -95°C and a copolymer poly(cyclooctadiene-co-cyclododecene) with twice less sp^2 carbons ($\sim 23\%$) has a lower T_g (-108°C). This copolymer, like some others, seems to appear as a serious candidate for an aging delay of low T_g hydroxytelechelic materials.

The influence of the composition and molar masses was first studied on the crystallization of the copolymers using pCOD-COE as model. As seen on Table III, the crystallinity of pCOD-COE was first observed to increase with the content of cyclooctene

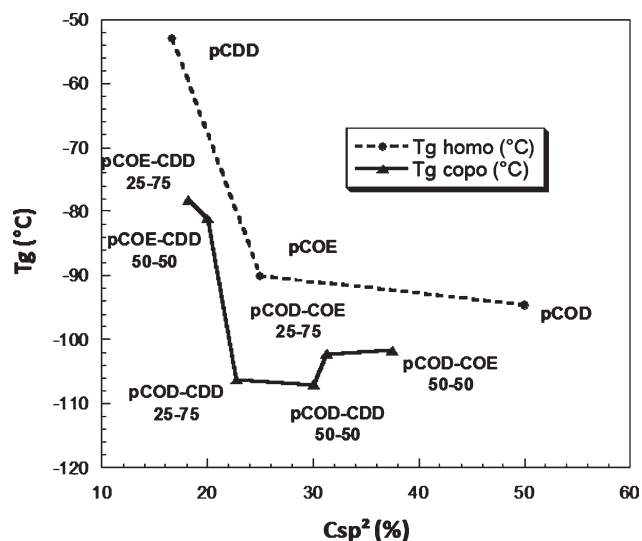


Figure 5 Copolymers T_g according to the Csp^2 proportion.

within copolymers having molar masses in the same range (entries 1 to 3). This result is consistent with the increase of the sp^3 carbons percentage, which is susceptible to cause chains organization. The important reduction of crystallinity in comparison with pCOE homopolymer (entry 4) is in agreement with a structural disorder. Runs 2, 5, and 6 show that copolymers with low molar masses are more likely to crystallize than high molar masses homologs. This is attributed to the highest propensity of small chains to move and thus to self-organize comparing to longer ones.

Aging tests were then carried out at 100°C and a close relation between the recombination reactions and crosslinking of the copolymers expressed by a critical time and the percentage of unsaturations present was obtained (Fig. 6). Decreasing gradually the sp^2 carbons percentage improves continuously the aging. Random copolymers based on cyclooctadiene, cyclooctene, and cyclododecene are much more interesting than polybutadienes homologs as

TABLE II
 T_g Values of Copolyalkenamers Measured by DSC (polymerizations in dichloromethane at 25°C, $[\text{Ru}]/[\text{olefin}] = 10^{-4}$)

Polyalkenamer	Csp^2 (%)	[M] (mol/L)	[M]/[CTA] ^a	Time (h)	Conv. (%)	\bar{M}_n exp (g/mol)	I_p	T_g (°C)
pCOD	50.00	3.8	25	3	70	7 900	1.7	-95
pCOD-COE 50-50	37.50	2.5	200	24	95	25 000	2.3	-102
pCOD-COE 25-75	31.25	2.5	200	24	95	19 000	2.0	-100
pCOD-CDD 50-50	30.00	3.3	270	3.5	55	8 600	1.6	-107
pCOE	25.00	3.7	25	0.25	43	21 300	2.3	-90
pCOD-CDD 25-75	22.72	3.0	25	12	62	8 700	1.9	-108
pCOE-CDD 50-50	20.00	4.4	432	3	65	28 900	1.8	-81
pCOE-CDD 25-75	18.18	4.0	364	2.5	55	16 500	1.9	-78
pCDD	16.67	3.0	18	5	60	17 500	1.2	-53

^a [monomer]/[butene diacetate]

TABLE III
 Synthesis and Characteristics of pCOD-COE Copolymers with Various Composition and Molar Masses (in dichloromethane at 25°C, [Ru]/[olefin] = 10⁻⁴)

Entry	Polyalkenamer	% Csp ² ^a (%)	[M] (mol/L)	[M]/ [CTA]	Time (h)	Conv. (%)	\bar{M}_n (g/mol)	Ip	T_m^b (°C)	Cristallinity ^b (%)
1	pCOD-COE 75-25	43.75	2.5	200	24	95	23 000	2.2	–	0
2	pCOD-COE 50-50	37.50	2.5	200	24	95	25 000	2.3	–24	5.3
3	pCOD-COE 25-75	31.25	2.5	200	24	95	19 000	2.0	5	8
4	pCOE	25.00	7.6	^c	1	15	24 000	1.9	38	14
5	pCOD-COE 50-50	37.50	3.6	15	16	80	5 000	2.1	–18	7.6
6	pCOD-COE 50-50	37.50	4.0	^c	0.5	18	50 000	2.3	–41	0.5

^a Csp² percentage = $n_{\text{Csp}^2}/n \times 100$.

^b Measured by DSC.

^c No butene diacetate added.

low glass transition temperature elastomeric materials precursors with high aging resistance are obtained.

CONCLUSIONS

Functionalized hydroxytelechelic copolyalkenamers based on cyclooctadiene, cyclooctene, and cyclododecene appear as elastomeric polymers characterized by very low glass transition temperatures, lower than –78°C. Depending on their composition, such copolyalkenamers are totally amorphous or can exhibit low cristallinity phase which melt at low temperatures. These materials show an improvement of resistance towards oxidation in air atmosphere. This behavior is characterized by a critical time corresponding to recombination reactions leading to crosslinking process activated at high temperature. This critical time increases with decreasing the unsaturations rate. These copolymers are considered as

interesting alternatives to hydroxytelechelic polybutadienes used as polyurethane precursors.

The authors of this paper would like to thank the DGA (Direction Générale de l'Armement) for their support in this research.

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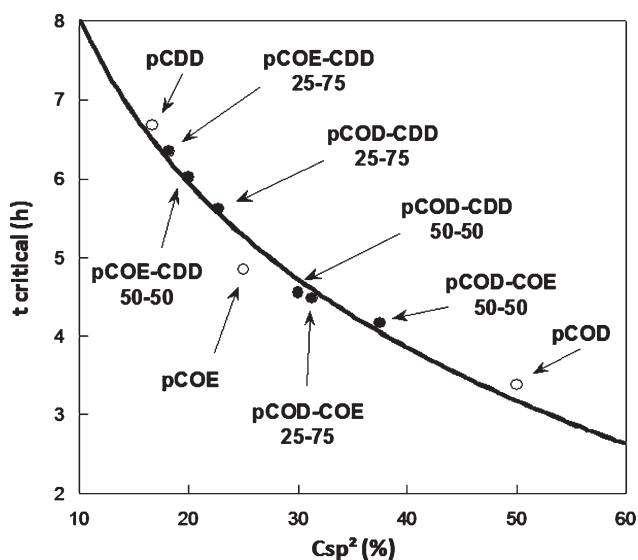


Figure 6 Critical time at 100°C according to 1,4-unsaturations proportion in the polymers.

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