



XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov

Oxidation and Structuring of Polydicyclopentadiene Thin Layers

Lyapkov, A.A.^{a*}, Gvozdkov, E.L.^a, Tarakanovskaya, A.N.^a, Tarnovskaya, O.D.^a,
Yakovleva, Y.S.^a

^a Tomsk Polytechnic University, Lenin Av., 30, Tomsk 634050, Russia

Abstract

It has been shown that polymeric film coatings derived from polydicyclopentadiene are subject to oxidation and structuring in air. Oxidation in air of double bonds in films gradually happens during several weeks and it comes amid an increase of adsorption band of carbonyl and hydroxyl groups in polymers infrared spectrums. Moreover, because of selective oxidation of cis-configured chains, structuring occurs around the double bonds in the polymer chain in polydicyclopentadiene films acquired by metathesis polymerization

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: Catalytic polymerization, polydicyclopentadiene thin layers, titanium tetrachloride, triisobutylaluminum, original Hoveyda–Grubbs II type catalyst, oxidation, cross-linking;

1. Introduction

An important task for chemical engineers is to solve the problem of recycling waste from manufacturing facilities. The usage of side products reduces the impact on the environment and can increase economic efficiency of the production.

Dicyclopentadiene contained in various particles of liquid products of pyrolysis has a system of olefinic bonds and strained cycles. It is quite a reactive compound. During dicyclopentadiene polymerization, depending on the type of chosen catalytic system¹⁻⁶, there are macromolecules formed with olefinic bonds in the main chain or

* Corresponding author. Tel.: +7-906-954-3336.
E-mail address: alexdes@tpu.ru

sidechains. The high unsaturation of dicyclopentadiene-based polymers predefines their tendency for oxidative and structural transformations in the thin layer⁷. However, a means of getting polydicyclopentadiene significantly influences this process determining the oxidation and structuring rate and process.

2. Experiment

Dicyclopentadiene polymerization in toluene solution was carried out in the reaction vessel, which was an ideal mixing reactor of 100 ml². The initiators were a catalytic complex of titanium tetrachloride with triisobutylaluminum in mole ratio 1:1, and an original Hoveyda–Grubbs II type catalyst⁸.

Dicyclopentadiene produced by Hangzhou Uniwise International Co., Ltd. with 99% base material content was cleared from stabilizer by distillation under reduced pressure of ~6.6 kPa.

Toluene was dehydrated by the known procedure⁹.

Titanium tetrachloride with 99.9% base material content and the density of 1.727 g/cm³ was used without additional clearing. Triisobutylaluminum (AliBu₃) was used as a solution in toluene with the concentration of 0.243 g/cm³. Working solution was prepared by diluting the main one with dry solvent until the needed concentration was achieved. All the procedures with TiCl₄ and AliBu₃ were carried out in a Mbraun LabStar glove box with argon atmosphere.

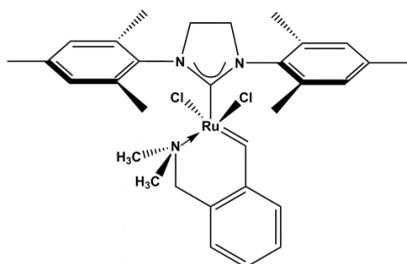
Infrared spectrums were registered using infrared Fourier spectrometer Thermo Electron Corporation NICOLET 5700 in the range 600–4000 cm⁻¹.

3. Results and discussion

Dicyclopentadiene polymerization under the complex of TiCl₄: AliBu₃ was carried out with sequenced adding of catalytic system components to the monomer solution in toluene with the concentration of 1.45 mol/l. The concentration of the catalytic system of TiCl₄:AliBu₃ (1:1) equaled 1.0710⁻³ mol/l.

It is obvious that there is cationic polymerization of dicyclopentadiene in this case as well as with just TiCl₄¹ or the catalytic system TiCl₄: AlEt₂Cl (1:1)^{2,3}.

Ruthenium complex (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro-(ortho-N,N-dimethylaminomethyl-phenylmethylene)-ruthenium⁷ soluble in the monomer and in toluene at room indoor temperature was the catalyst of metathesis dicyclopentadiene polymerization:



It is stable during storage, resistant to oxygen and air moisture, so it does not require inert atmosphere. The catalyst concentration was 1.07·10⁻³ mol/l (mole ratio of the monomer to the catalyst was 1400:1).

During metathesis dicyclopentadiene polymerization the estimated amount of the original Hoveyda–Grubbs II type catalyst dissolved in toluene was added to the monomer solution.

The derived polymers were soluble in aromatic and chlorinated hydrocarbons that are used to get glossy transparent films. However, in course of time during air storage polydicyclopentadiene films get dark, their solubility gets worse because of the oxidation of double bonds and formation of cross-linking in the polymer structure.

Oxidation in air of double bonds in the films is gradual and comes amid the intensity increase of the absorption band of carbonyl and hydroxyl groups in infrared spectrums of polymers (fig. 1).

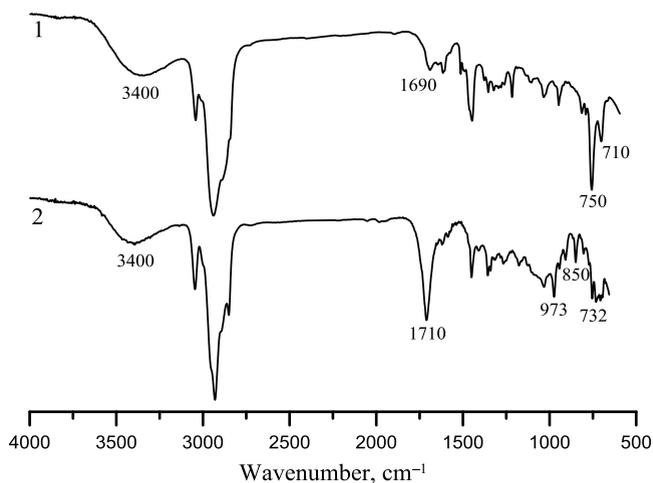


Fig. 1. The infrared spectrum of the dicyclopentadiene polymers films from the toluene solution under the catalytic system TiCl_4 - AliBu_3 (1) and under the original Hoveyda-Grubbs II type catalyst (2), 25 hours after synthesis, the thin layers on KBr.

A wide band at 3400 cm^{-1} belongs to valence vibrations of hydroxyl groups near various carbon atoms in the main chain of polymers. In infrared spectrum there is also an increase of intensity of absorption of deformation vibrations of carboxyl groups at 1690 cm^{-1} for polydicyclopentadiene from cationic polymerization (curve 1, fig. 1), and 1710 cm^{-1} for polydicyclopentadiene from metathesis polymerization (curve 2, fig. 1). Apart from this, in infrared spectrums the intensity of adsorption of ether groups also increases (a wide band $\sim 1030\text{--}1080\text{ cm}^{-1}$).

It can be seen in figure 1 that there are distinctive differences in the structure of polymers from cationic (curve 1) and metathesis (curve 2) polymerization. So, in the range $700\text{--}770\text{ cm}^{-1}$ the position and the quantity of bands of CH-bonds deformation vibrations show that there is a six-membered ring in the products of cationic polymerization (curve 1, fig. 1), while there is only a five-membered ring in the products of metathesis polymerization (curve 2, fig. 1).

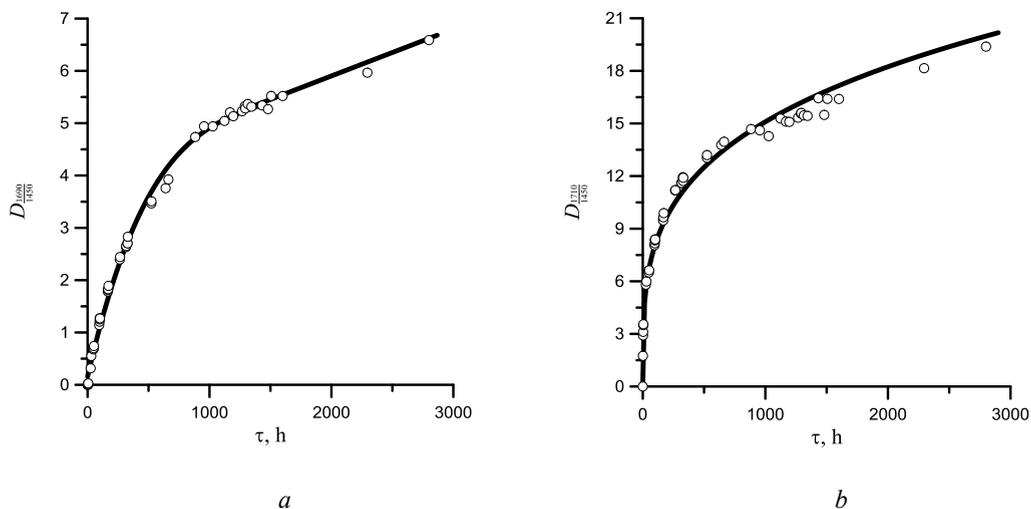


Fig. 2. The correlation of adsorption bands at 1690 and 1450 cm^{-1} for polydicyclopentadiene from cationic polymerization (a) and 1710 and 1450 cm^{-1} for polydicyclopentadiene from metathesis polymerization (b), and the time of film exposure to the air.

In the range of products of metathesis polymerization (curve 2, fig. 1) there are vibrations bands of *cis*- and *trans*-isomerism at the double bonds in the polymeric chain (correspondingly 732 and 974 cm^{-1}) which are not found in the range of the products of cationic polymerization (curve 1, fig. 1).

The oxidation kinetics of the polydicyclopentadiene films in air was studied using the intensity dynamics of deformation vibrations adsorption of carboxyl groups and valence vibrations of hydroxyl groups. In figure 2 there are kinetic curves of polydicyclopentadiene oxidations in the form of correlations of the changes of relative deformation vibrations intensity in the carboxyl group and the time of film exposure to the air.

The correlation in figure 2 shows that the oxidation is at its maximum on day 20 after which the process becomes stable and acquires a constant rate.

Figure 3 shows kinetic curves of polydicyclopentadiene oxidation in the form of a correlation of the changes of relative valence vibrations intensity in hydroxyl group and the time of film exposure to the air.

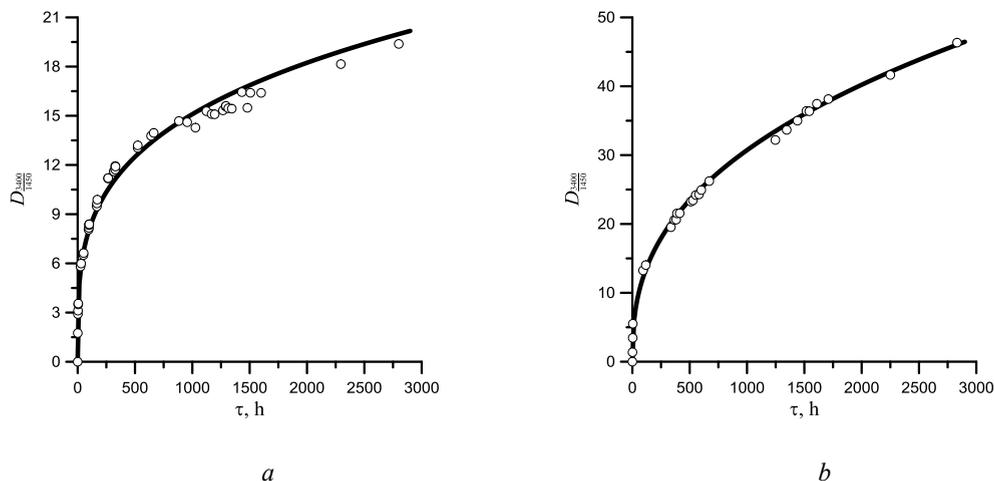


Fig. 3. The correlation of adsorption bands at 3400 and 1450 cm^{-1} for polydicyclopentadiene from cationic polymerization (a) and for polydicyclopentadiene from metathesis polymerization (b) and the time of film exposure to the air.

It can be seen that it is the same as in the previous case (fig. 2). Probably it is because the penetrability of partially oxidated films decreases, and further on the diffusion of oxygen into the film limits this process. This leads to the change in the rate of the process registered on the curves in figures 2 and 3. In fact, considering that along with polydicyclopentadiene thin layers oxidation there is structuring and formation of additional cross-linking between macromolecular chains. Then it is clear that this process should lead to a change in films physical properties and their penetrability for air oxygen.

The change in the adsorption intensity of *cis*- and *trans*-isomerism bands at 732 and 973 cm^{-1} show how structuring processes develop in polydicyclopentadiene film from metathesis polymerization.

The common correlation of optical density (D) of adsorption bands at 732 and 1450 cm^{-1} and 973 and 1450 cm^{-1} in the infrared spectrum of polydicyclopentadiene received using metathesis polymerization and the time of film exposure to the air (τ) is in figure 4.

If relative band intensity of *cis*-isomerism of a polymeric chain around the olefinic bond rapidly decreases in course of time (fig. 4, a), then the intensity of *trans*-isomerism bond decreases at a lower rate (fig. 4, b). This trend leads to that mostly chains with *trans*-configuration towards the olefinic bond remain in the polymeric chain in course of time.

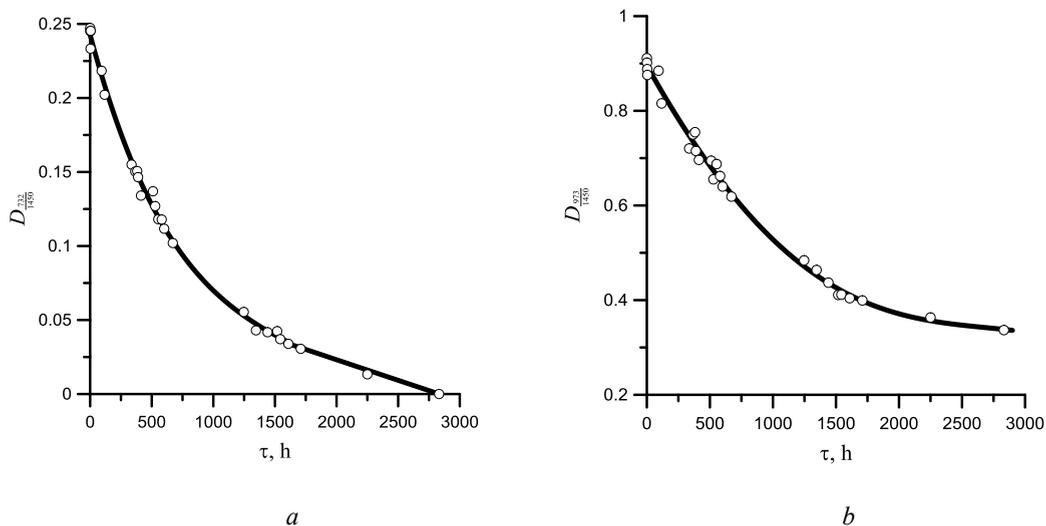


Fig. 4. The correlation of adsorption bands at 732 and 1450 cm^{-1} (a) and 973 and 1450 cm^{-1} (b) in the infrared spectrum of polydicyclopentadiene with the time of film exposure to the air.

As oxidation happens, the number of chains with *cis*-configuration towards the olefinic bond drops nearly to none (fig. 4, a).

Nominal quantity of chains of *trans*-configuration in the polymeric chain (fig. 4, b) also decreases. However, this decrease is not as rapid as the decrease of vibrations intensity of *cis*-configuration chains (fig. 4, b).

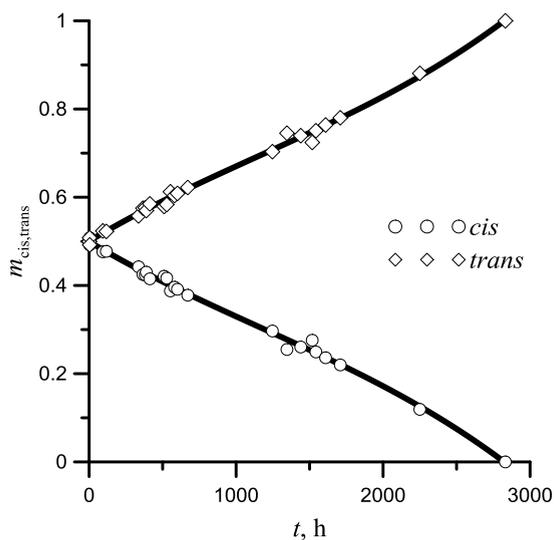


Fig. 5. The correlation between the nominal content of chains of *cis*- and *trans*-configurations in the polymeric chain and time

If supposed that the initial content of chains of *cis*- and *trans*-configuration in relation to the double bonds in the polymeric chain is equal, then gradually in course of time in the polymeric chain there would only be left bonds having *trans*-configuration because of oxidation and structuring (fig. 5).

4. Conclusion

Polymeric film coating made of polydicyclopentadiene from cationic and metathesis polymerization in the air undergoes oxidation and structuring. In air, oxidation of double bonds in films is gradual during several weeks and comes amid an increase of absorption band of carbonyl and hydroxyl groups in the infrared spectrums of oligomers. At the same time, structuring and isomerism occur in films. This leads to the change of films physical properties, in particular to a decrease in films permeability for air oxygen.

References

1. Peng YX, Liu JL, Cun LF. Microstructure of Polymers Obtained by Cationic Polymerization of endo-Dicyclopentadiene. *J. Polym. Sci.* 1996; **34**, 17:3527-3530.
2. Lyapkov AA, Bondaletov VG, Mel'nik (Ionova) EI, Ogorodnikov VD. Investigation of dicyclopentadiene polymerization in the presence of catalyst systems based on $TiCl_4$. *Izvestiya Tomskogo politekhnicheskogo universiteta* 2013; **322**, 3:105-112.
3. Qian Y, Dono K, Huang J, Ma H. Ring-Opening Metathesis Polymerization of Dicyclopentadiene Catalyzed by Titanium Tetrachloride Adduct Complexes with Oxygen-Containing Ligands. *J. App. Polym. Sci.* 2001; **81**, 3:662-666.
4. Pacreau A, Fontanille M. Linear polymerization of endo-dicyclopentadiene initiated by metathesis catalysts. *Makromol. Chem.* 1987; **188**, 11:2585-2595.
5. Dono K, Huang J, Ma H, Qian Y. Ring-Opening Metathesis Polymerization of Dicyclopentadiene Catalyzed by Titanium Tetrachloride Adduct Complexes with Nitrogen-Containing Ligands. *J. App. Polym. Sci.* 2000; **77**, 14:3247-3251.
6. Rule JD, Moore JS. ROMP Reactivity of endo- and exo-Dicyclopentadiene. *Macromolecules* 2002; **35**, 21:7878-7882
7. Ionova EI, Lyapkov AA, Bondaletov VG. Oxidation and structuring of oligomers based on dicyclopentadiene. *Izvestiya Tomskogo politekhnicheskogo universiteta* 2011; **318**, 3:101-105.
8. Kolesnik VD, Ashirov RV, Shcheglova NM, Novikova ES, Jakimov RV, Nosikov AA, et al. Ruthenium Catalyst of Metathesis Dicyclopentadiene Polymerization and Method of its Generation. **Patent RU 2409420 C1**; 2011.
9. Weissberger A, Proskauer ES, Riddick JA, Toops EE. *Organic Solvents. Physical Properties and Methods of Purification*. New York: Interscience Publishers; 1955. 435 p.