Macromolecules **1989**, *22*, 2129–2130

Soluble Catalysts for Syndiotactic Polymerization of Styrene

Adolfo Zambelli,* Leone Oliva,[†] and Claudio Pellecchia

Dipartimento di Fisica, Università di Salerno, I-84081 Baronissi (SA), Italy.

Received July 25, 1988

ABSTRACT: Several titanium and zirconium compounds have been tested in the presence of methylalumoxane as catalysts for syndiotactic polymerization of styrene. Titanium compounds having oxidation numbers as low as 2 are suitable catalysts. The ligands of titanium have little relevance, if any, in the performances of the catalytic system. Tetrabenzylzirconium gives a less active catalyst than tetrabenzyltitanium, and the crystalline polymer obtained is less stereoregular.

A variety of titanium and zirconium compounds, in the presence of methylalumoxane (MAO), promote syndiotactic polymerization of styrene.[1-4] In this paper we report a comparison of the results obtained when testing catalytic systems prepared by using different transition-metal compounds under otherwise identical reaction conditions. The transition-metal compounds used, the reaction conditions, and the results are summarized in Table I. The polymerization procedure and the description of the various operations are reported in the Experimental Section.

Examining the results of Table I, one observes the following:

(1) The ligands of the transition-metal compounds have a modest influence on the performance of the catalysts. In fact, the yield and the amount of highly syndiotactic acetone–insoluble fractions are not very different from each other in the polymers resulting from runs 1–3.

(2) Ti(IV), Ti(III), and Ti(II) give active catalysts (runs 1–5). In the presence of Ti(0) catalyst, only traces of atactic material are produced (run 6).

(3) $Zr(bz)_4$ gives a less active catalyst than $Ti(bz)_4$ (compare runs 1 and 7).

(4) The acetone-insoluble fractions of the polymers obtained in the presence of Ti are more stereoregular than those obtained in the presence of Zr. On the other hand, the acetone-soluble fractions of the polymers obtained in the presence of Ti are stereoirregular, while those of the polymers obtained in the presence of Zr are predominantly syndiotactic.[2]

(5) The molecular weight distribution of the polymer prepared in the presence of Zr follows the Schulz–Flory equation. The molecular weight distribution of the polymers prepared with Ti is somewhat broader and varies depending on the titanium compound used. It is worth noticing that the raw polymers include stereoirregular acetone-soluble fractions, which obviously arise from a different mechanism[5] and that, as reported previously,[5] the molecular weight distribution is noticeably sharper for the extraction residues.

Finding 1 suggests that the ligands of the transition-metal compounds are completely removed by the reaction with MAO. Since they only marginally affect the stereoregularity and the yield, they are probably not in the coordination sphere of the transition metal of the active species.

Table I
Polymerization Conditions and Results in the Presence of Different Catalytic Systems[a]

run	transition-metal compd[b]	yield, g	insoluble fraction,[c] %	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	$Ti(bz)_4$	0.82	93	153	4.6
2	$Ti(O\text{-}bu)_4$	0.57	91	344	11.8
3	$TiCpCl_3$	0.73	91	96	2.8
4	$Ti(acac)_3$	0.30	89	327	13.3
5	$Ti(ph)_2$	0.11	88	370	9.6
6	$Ti(bipy)_3$	0.01[d]	0		
7	$Zr(bz)_4$	0.25	56	9	2.2

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; MAO, 2.5 mmol (based on Al); transition-metal compound, 2.5 × 10^{-5} mol; $T = 50$ °C; time, 100 min. [b] Here and in the text, bz = benzyl, O-bu = *n*-butoxide, Cp = cyclopentadienyl, acac = acetylacetonate, ph = phenyl, and bipy = bipyridyl. [c] In boiling acetone (see Experimental Section). [d] Atactic polymer (by NMR).

Finding 2 suggests that the oxidation number of the titanium of the active species might be lower than 4 and higher than 0. Actually, considering that reaction with MAO can only reduce the oxidation number of the transition metal and that $Ti(bipy)_3$ produces only stereoirregular polymers while $Ti(ph)_2$ still promotes syndiotactic polymerization, one would conclude that the oxidation number of Ti of the active species should be 2 or 1. However, since oxidative addition reactions involving, e.g., the monomer or even the solvent, cannot be excluded a priori, oxidation number 3 cannot be ruled out at this stage.

Finding 3 accordingly suggests that the lower activity of $Zr(bz)_4$ in comparison with $Ti(bz)_4$ may be due, at least in part, to the higher stability of oxidation number 4 for Zr. As a consequence, reaction with MAO should afford a lower amount of active species.

Finding 4 could be due to a more crowded coordination sphere around Ti having a smaller radius in comparison with Zr. Finding 5, i.e., the sharp distribution of the molecular weights of the polymer obtained in the presence of $Zr(bz)_4$, strongly suggests that the catalyst is homogeneous.[5] The broader distribution observed in the presence of Ti could be explained by considering that some intermediates of the reaction with MAO may be chain-transfer agents, consumed during the polymerization. This hypothesis could justify the deviation from the Schulz–Flory equation even in the presence of a homogeneous catalyst. On the other hand, the hypothesis does not appear unreasonable when considering the variety of organometallic species possibly present as a result of the interaction of Ti and MAO.

Experimental Section

Toluene was distilled under nitrogen atmosphere after refluxing over potassium for 48 h. Styrene was distilled under reduced pressure over CaH_2 before use. MAO was prepared as previously reported.[6] Titanium tetrabutoxide was purchased from Aldrich. Tetrabenzyltitanium,[7] cyclopentadienyltrichlorotitanium,[8] titanium triacetylacetonate,[9] diphenyltitanium,[10] tris(bipyridyl)titanium,[11] and tetrabenzylzirconium[7] were prepared as described in the literature.

All the polymerization runs were carried out, as previously described,[5] introducing sequentially toluene, MAO, styrene, and the transition-metal compound, in the amounts specified in Table

---

[†] Present address: Dipartimento di Chimica, Università di Napoli, Via Mezzocannone 4, I-80134 Napoli, Italy.

0024-9297/89/2222-2129$01.50/0

I, to 100-mL stirred glass flasks thermostated at 50 °C. Polymers were coagulated with acidified methanol and worked out as usual. Polymer samples were fractionated with boiling acetone in Kumagawa-type extractors. The extraction residues of polymers obtained in runs 1–5 are highly syndiotactic (fraction of rr triads, determined by ^{13}C NMR, >98%) and melt at 260 °C. The extraction residue of the polymer produced in run 7 has a content of rr triads of 88% and melt at 220 °C.

Molecular weights were determined on the raw polymers by GPC in 1,2-dichlorobenzene at 135 °C using a Waters 150-C apparatus.

Acknowledgment. Financial support by Ministero della Pubblica Istruzione and by Consiglio Nazionale delle Ricerche is gratefully acknowledged. Thanks are due to E. Comunale for technical assistance.

Registry No. Ti(bz)$_4$, 17520-19-3; Ti(O-bu)$_4$, 5593-70-4; TiCpCl$_3$, 1270-98-0; Ti(acac)$_3$, 14284-96-9; Ti(ph)$_2$, 14724-88-0; Zr(bz)$_4$, 24356-01-2; syndiotactic polystyrene, 28325-75-9.

References and Notes

(1) Ishihara, N.; Kuramoto, M.; Uoi, M. *Eur. Pat. Appl.* 210615, 1987; *Chem. Abstr.* **1987**, *106*, 177084p.

(2) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *19*, 2465.

(3) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.

(4) Soga, K.; Yu, C. H.; Shiono, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 351.

(5) Oliva, L.; Pellecchia, C.; Cinquina, P.; Zambelli, A. *Macromolecules*, in press.

(6) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703.

(7) Zucchini, V.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

(8) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

(9) Chakravarti, B. N. *Naturwissenschaften* **1958**, *45*, 286.

(10) Latjaeva, V. N.; Razuvaev, G. A.; Malisheva, A. V.; Kiljakova, G. A. *J. Organomet. Chem.* **1964**, *2*, 388.

(11) Herzog, S.; Taube, R. *Z. Anorg. Allg. Chem.* **1960**, *306*, 159.

Synthesis and Optical Properties of a New Class of Polyamides Containing Reactive Diacetylene Groups

H. W. Beckham and M. F. Rubner*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received August 22, 1988;
Revised Manuscript Received October 25, 1988

ABSTRACT: New polyamides containing reactive diacetylene groups in their repeat structures were synthesized from a diacetylene diacid chloride and two different diamines by using interfacial polymerization techniques. Thermal analysis and ^{13}C NMR spectroscopy were used to estimate the extent of conversion of the diacetylene groups to polydiacetylene network chains upon exposure to electron beam radiation in the solid state. The diacetylene groups contained in a polyamide based on an aliphatic diamine were found to be more reactable than those incorporated in a polyamide based on an aromatic diamine. The cross-polymerized polyamide–diacetylenes were found to exhibit reversible thermochromic behavior during temperature cycling which occurs with complete retention of hydrogen bonds and without any hysteresis effects. The thermochromic reversibility of these materials was attributed to the strongly hydrogen-bonded chain segments pendent to the newly formed polydiacetylene chains.

I. Introduction

This paper describes the preparation and properties of several new polyamides that contain the reactive diacetylene group as part of their repeat structure. The goal of this research is to identify new types of chemistry that can be utilized to modify and enhance selected properties of fiber-forming polymers after they have been processed into highly anisotropic forms. In order to accomplish this goal, it is necessary to introduce reactive groups into the polymer chain that remain dormant during processing but that can also be readily activated in the solid state to produce the desired changes in properties. We are currently focusing on the chemistry of the diacetylene group, which, as indicated below, provides a novel way to dramatically modify the mechanical and optical properties of the host polymer system.

The solid-state polymerization of diacetylene monomers, $RC{\equiv}CC{\equiv}CR$, has been well documented in the literature.[1] A unique feature of this polymerization is that it often proceeds as a homogeneous single-phase process taking place without destruction of the crystalline order of the original monomer lattice. The resultant fully extended polydiacetylene chains, $[-(R)C{=}C(R)C{\equiv}C-]_x$, exhibit many novel linear[2] and nonlinear[3] optical properties, all of which are a direct consequence of the one-dimensional nature of the polydiacetylene conjugated backbone and its highly delocalized electronic states. This chemistry can be initiated using actinic radiation, ionizing radiation, or, in some cases, simple thermal treatment, making it ideal for postprocessing modification schemes.

As has been previously demonstrated,[4-10] the reactive diacetylene group can be readily incorporated into many different polymeric structures, $[-C{\equiv}CC{\equiv}CR-]_x$, making it possible to synthesize a wide variety of fiber- and film-forming polymers with tunable mechanical and optical properties. The controlled solid-state cross-polymerization of polymers containing diacetylene groups is therefore an extremely attractive method for the systematic postsynthesis modification of the mechanical and optical properties of polymeric materials. This chemistry provides a novel way to introduce well-defined, nonrandom cross-links into a polymeric material often times without disruption of the packing and order of the polymer chains. In addition, since the resultant cross-links are actually conjugated polydiacetylene chains, the material develops all of the novel optical properties characteristic of the polydi-

0024-9297/89/2222-2130$01.50/0