Macromolecules
COMMUNICATION TO THE EDITOR
pubs.acs.org/Macromolecules

Preparation of Functional Polyethylenes by Catalytic Copolymerization

Jean-Christophe Daigle, Laurence Piche, and Jerome P. Claverie*

Department of Chemistry, Quebec Center for Functional Materials, UQAM, Succ Centre Ville CP8888, Montreal, H3C3P8 Quebec, Canada

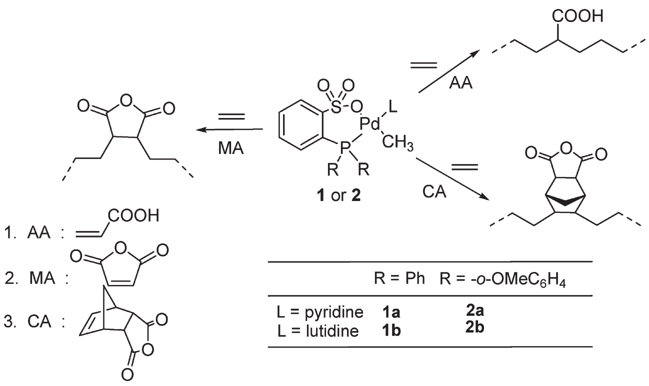
Supporting Information

The physical properties of polyethylene (PE) can be drastically altered by careful manipulation of its microstructure and particularly by controlling the length and distribution of alkyl branches along the chain. Instead of alkyl chains, it would be desirable to introduce low amounts of polar groups because they are expected to greatly impact the toughness, flexibility, crack resistance, gas permeability, miscibility, adhesion, and paintability of PE.[1] These copolymers are also of prime importance for the formation of nanocomposites since the presence of polar groups enhances compatibility between the polymeric matrix and the dispersed charge.[2] However, catalytic polymerization of readily available polar monomers is still one of the major challenges in the field of olefin polymerization.[3] Among all polar monomers, those bearing easily functionalized groups such as carboxylic acid and anhydrides would offer a unique opportunity for the direct preparation of functional PEs.

Polymers bearing anhydride functionalities can be prepared by reactive extrusion of molten PE in the presence of maleic anhydride (MA) and a radical initiator. This radical process not only grafts the anhydride as a pendant group but also generates several undesirable side reactions such as chain scission and chain branching.[4] Radical copolymerization of ethylene with acrylic acid (AA) or methacrylic acid yields ionomers,[5] that is to say, thermoplastics containing acid groups converted to metal salts which act as physical cross-links. These commercially important polymers are used in a variety of applications, including orthodontics and prosthetics, as films, adhesive layers in foil/paper containers, and as constituents of items such as golf balls and bowling pins. We recently demonstrated that linear copolymers of ethylene and AA exhibit higher crystallinity and melting points than their branched counterparts.[6] Furthermore, in water they self-assemble into thermosensitive nanoparticles. These copolymers were prepared by catalytic copolymerization of ethylene with *tert*-butyl acrylate followed by deprotection of the ester. Clearly, it would be advantageous to prepare these copolymers by direct copolymerization with AA.

We have probed the preparation of functional PE by catalytic copolymerization of ethylene with AA, MA, and carbic anhydride (CA, 5-norbornene-*endo*-2,3-dicarboxylic anhydride) using Pd-based well-defined catalysts **1** or **2** (Scheme 1). The choice of these catalysts is motivated by the fact that Pd phosphine aryl sulfonates allow for the copolymerization of a wide range of monomers, such as acrylonitrile,[7] vinyl ethers,[8] vinyl esters,[9] vinyl fluoride,[10] acrylates,[11−14] norbornenes,[15,16] styrenes,[17] vinyl ketones,[17] acrylamides,[18] *N*-vinylpyrrolidone,[18] vinyl sulfones,[19] and carbon monoxide in a nonalternated fashion.[20] During the preparation of this paper, it was also reported that Pd phosphine aryl sulfonates afford the copolymerization of ethylene and AA.[21]

Scheme 1. Catalytic Copolymerization of AA, MA, and CA with Ethylene



In our hands, catalysts **1** or **2** are not able to insert significant quantities of MA. Activation by a Lewis acid has been shown to be efficient to remove the coordinated pyridine or lutidine, generating a more active catalyst.[17,22] Accordingly, both **1a** and **2a** in the presence of 5 equiv of BF_3 are able to incorporate MA (Table 1). On the contrary, insertion of CA or AA does not require Lewis acid activation. Catalyst **1a** is able to incorporate CA with no significant decrease of the molecular weight or lowering of the activity relative to the homopolymerization of ethylene (values for homopolymerization can be found in ref 14). In stark contrast, copolymerization of AA is slow, giving polymers in low yield. After heating **1b** (c = 90 mmol/L) with 2 equiv of AA in $CDCl_3$ for 8 h at 50 °C, the catalyst remained intact (no insertion product detected), indicating the poor initiation efficiency of these catalysts. Surprisingly, lutidine was not trapped by AA and remained coordinated to the Pd. This experiment also emphasizes the exceptional stability of these catalysts toward functional groups such as carboxylic acids. The AA-containing polymers proved to be difficult to purify and to analyze due to the formation of intramolecular H-bonds (entry 11) which

Received: January 18, 2011
Revised: February 23, 2011
Published: March 04, 2011

Table 1. Catalytic Copolymerization of Ethylene with Functional Monomers (FM)

entry	FM	Cat.	P (psi)	T (°C)	solvent	[Mon] (mol/L)	[Cat.] (μmol/L)	TON (/h)	yield (mg)	x (mol %)[a]	M_n[b] (g/mol)	PDI[b]	T_m[c] (°C)	crystallinity[c]
1	MA	**2a**[d]	320	100	tol−Et$_2$O[e]	1.1	190	500	260	4	1800	1.7	72	38
2	MA	**2a**[d]	100	100	tol−Et$_2$O	1.1	190	580	320	2	2700	1.4	116	36
3	MA	**1a**[d]	300	100	tol	1.1	180	140	80	9	2800	1.7	84	37
4	CA	**2a**	100	75	tol	0.7	390	560	140	11	8000	1.7	52[g]	1.5
5	CA	**2a**	110	75	tol	0.1	210	1500	190	7	nd[f]	nd	89	15
6	CA	**2a**	115	90	tol	0.6	380	10 700	800	10	3800	1.5	nd[g]	nd
7	AA	**1b**	100	75	tol	0.3	380	3600	60	6	nd	nd	109	28
8	AA	**1b**	100	95	tol	1.9	380	840	60	1.5	nd	nd	115	nd
9	AA	**1b**	100	85	THF	0.6	380	180	40	5	nd	nd	100	25
10	AA	**1b**	100	95	THF	0.4	380	510	100	4	nd	nd	99	22
11[h]	AA	**2a**	100	95	tol	0.6	380	220	60	nd	nd	nd	nd	nd

[a] The mol % composition of the copolymer was determined by ^{1}H NMR. [b] Determined by GPC at 160 °C in trichlorobenzene. [c] Determined by DSC. [d] Five equiv of BF$_3$ was added. [e] tol: toluene. Mixtures tol:Et$_2$O were 70:30 vol %. [f] Not determined (no suitable conditions found for GPC of AA containing copolymers). [g] Polymer nearly entirely amorphous. [h] This polymer was isolated in dry MeOH and could not be redissolved for analysis.

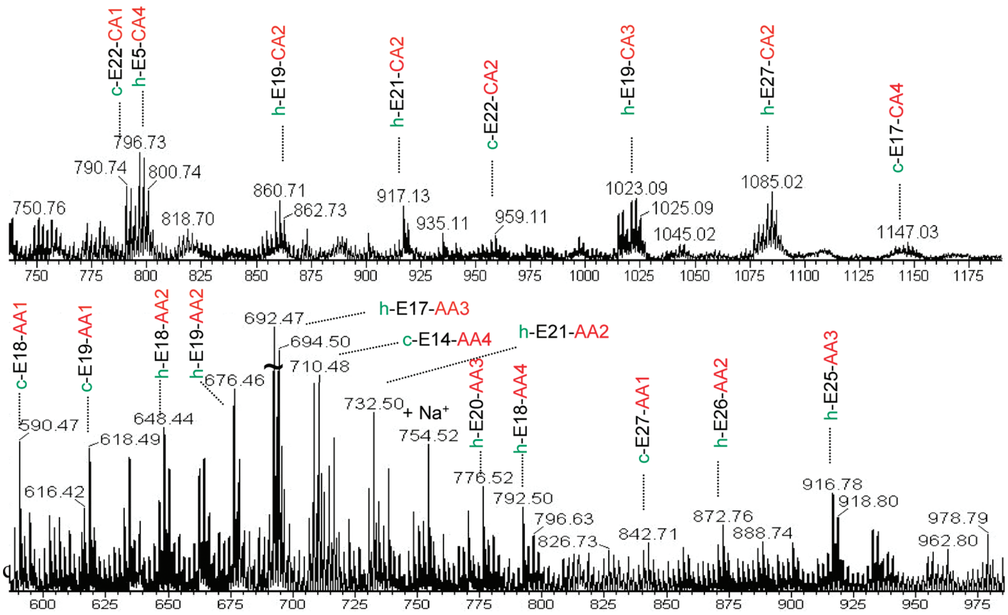


Figure 1. MALDI-TOF MS of copolymers of ethylene E and AA or CA (the numbers corresponding to the polymerization degree). Chains are either initiated by a hydride (h) or a methyl group (c) and are terminated by an unsaturation.

prevent the polymer from being redissolved.[6] Precipitation of the polymer in MeOH:water 90:10 warranted that the polymer could later be redissolved in chlorinated solvents at high temperature. Molar incorporations were assessed by ^{1}H NMR. Molar insertions of CA were relatively high (Table 1) even when low monomer concentrations were used, which is consistent with the fact that catalysts **1a** and **2a** are prone to insert monomers in the norbornene family.[15,16] Incorporation of MA (in a toluene−Et$_2$O solution) proved to be more difficult, as large amounts were necessary for low molar insertions, resulting in the formation of low-molecular-weight polymers (as shown by GPC) with a majority of terminal MA end groups (entries 1 and 2).

When MA was suspended in toluene, it was essentially inserted in a main chain position, with 7 MA units per chain (entry 3, calculated from x mol % and M_n), vs ~1 MA per chain for polymers prepared in the presence of Et$_2$O. This drastic solvent effect on comonomer insertion can be paralleled to the solvent effect on molecular weight distribution observed with related Pd aryl sulfonates.[23] For CA and AA, end groups were in too a low concentration to be quantified by ^{1}H NMR, and only main-chain polar units are detected. Main-chain incorporation for these copolymers was also confirmed by MALDI-TOF MS (Figure 1). Interestingly, both chains starting by a hydride and by a methyl group were observed, which demonstrates the capacity for the catalyst to reinitiate a chain after β-hydride abstraction. Low melting points and crystallinity content were also further evidence of main chain incorporation.

These copolymers are essentially linear, with only Me branches observed in low amounts (<10 branches per 1000C). For copolymers of CA and ethylene, NOE transfer experiments indicate that bridge protons strongly transfer magnetization to main chain methine protons, putatively demonstrating that the Pd alkyl insertion occurred across the *endo* face of CA. This contrasts with the usual *exo* face insertion seen for most norbornene polymerizations with Pd complexes.[24] This observation could be explained by the chelating effect of the succinate moiety on the *endo* face. In conclusion, we have outlined the preparation of copolymers of ethylene bearing acid and anhydride functionalities by direct catalytic copolymerization. These polymers structures may be easily modified in order to create a variety of functional materials

■ ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and characterization (^{1}H, ^{13}C NMR, MALDI-TOF MS). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: claverie.jerome@uqam.ca.

■ ACKNOWLEDGMENT

This work was supported by NSERC and FQRNT. J.C.D. and L.P. thank NSERC for a Research Fellowship.

■ REFERENCES

(1) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479–1493.

(2) Hippi, U.; Ristolainen, N.; Logfren, B.; Seppala, J. In *Polyolefin Composites*; Nwabunma, D., Kyu, T., Eds.; John Wiley & Sons: Hoboken, NJ, 2008.

(3) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268. (b) For a review, see: Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244.

(4) Yang, L.; Zhang, F.; Endo, T.; Hirotsu, T. *Macromolecules* **2003**, *36*, 4709–4718.

(5) *Ionomers: Synthesis, Structure, Properties and Applications*; Tant, M. R., Wilkes, G. L., Eds.; Chapman & Hall: London, 1997.

(6) Kryuchkov, V. A.; Daigle, J.-C.; Skupov, K. M.; Claverie, J. P.; Winnik, F. M. *J. Am. Chem. Soc.* **2010**, *132*, 15573–15579.

(7) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949.

(8) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946–8947.

(9) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 146060–14607.

(10) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450–15451.

(11) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745.

(12) Guironnet, D.; Roesle, P.; Runzi, T.; Gottker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2008**, *131*, 422–423.

(13) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033–2038.

(14) Skupov, K.; Hobbs, J.; Marella, P.; Conner, D.; Golisz, S.; Goodall, B.; Claverie, J. *Macromolecules* **2009**, *42*, 6953–6963.

(15) Liu, S.; Borkar, S.; Newsham, D.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 210–216.

(16) Skupov, K. M.; Marella, P. R.; Hobbs, J. L.; McIntosh, L. H.; Goodall, B. L.; Claverie, J. P. *Macromolecules* **2006**, *39*, 4279–4281.

(17) Borkar, S.; Newsham, D. K.; Sen, A. *Organometallics* **2008**, *27*, 3331–3334.

(18) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309–2310.

(19) Bouilhac, C.; Runzi, T.; Mecking, S. *Macromolecules* **2010**, *43*, 3589–3590.

(20) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964–965.

(21) Runzi, T.; Frohlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690–17691.

(22) Guironnet, D.; Caporaso, L.; Neuwald, B.; Goettker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418–4426.

(23) Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2009**, *132*, 52–53.

(24) Goodall, B. In *Late Transition Metal Polymerization Catalysis*; Rieger, B., Baugh, L. S., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003; pp 101−154.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on March 4, 2011. The Supporting Information was revised and the corrected version was reposted on March 17, 2011.