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Syntheses of mono(1,3-oxazolin-2-yl)-terminated oligopropene macromonomers and novel polymers containing oligopropene side chains

Christof Wörner [1], **Joachim Rösch** [2], **Arthur Höhn** [2], **Rolf Mülhaupt** [1], *

[1] Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Str. 21, D-79104 Freiburg i. Br., Germany
[2] BASF AG, D-67056 Ludwigshafen, Germany

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Summary

Mono(1,3-oxazolin-2-yl)-terminated atactic oligopropene with M_n=710g/mol was derived in high yields from monoester-terminated oligopropene via reaction with 2-aminoethanol and subsequent $Ti(OC_4H_9)_4$-catalyzed dehydration at 180°C. Cationic bulk polymerization of this novel macromonomer, initiated with 2 mol% methyl-4-nitrobenzenesulfonate at 200°C, afforded high molecular weight poly[N-oligopropene-1-carbonyl-ethyleneimine]. Grafting of mono(1,3-oxazolin-2-yl)-terminated oligopropene with poly(ethene-co-methacrylic acid), containing 3 mol% methacrylic acid, by heating both components for 15minutes at 220°C yielded novel ethene copolymers containing 41wt% ester-amide-coupled oligopropene as side chains.

Introduction

Oligomers containing one polymerizable endgroup are well known as macromonomers which can be polymerized to form polymers containing oligomeric side chains. Living anionic and cationic polymerization and chemical modifications of various telechelics, e.g., oligoisobutylenes, represent synthetic methods of choice in macromonomer synthesis [1]. Much less is known about propene-based telechelics because modern industrial Ziegler-Natta-type catalysts do not afford living polypropene. While traditional catalysts were devleoped to produce high molecular weight isotactic polypropene, novel generations of metallocene-based catalysts give independent control on molecular weight and stereoregularity over a very wide range [2]. As a function of metallocene structure and ligand substitution patterns, it is possible to produce vinylidene-terminated oligopropenes in high yields with respect to transition metal. Such vinylidene-endgroups are readily converted into a variety of other functional groups which are useful intermediates in polymer synthesis [3-5]. For instance, acrylic oligopropene macromonomers are obtained when hydroxy-terminated oligopropenes, derived from vinylidene-terminated oligopropene, are esterified with methacylic acid. Free radical homo- and copolymerization of such macromonomers give acrylic polymers with pendent oligopropene chains [4,5]. Although 2-substituted 1,3-oxazolines have been recognized as attractive monomers, which can be polymerized via ring-opening involving living cationic polymerization [6], nucleophilic substitution [7], or zwitterionic polymerization [8], their potential in macromonomer synthesis has not yet been fully exploited. For example, Kobayashi and Saegusa [9] described cationic polymerization of oxazoline-terminated oligoethyleneoxide in the presence of $BF_3 \cdot OEt_2$ initiator, which in acetonitrile solution afforded merely oligomers

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* Corresponding author

exhibiting an average degree of polymerization of approximately five. Purpose of our research has been to prepare novel mono(1,3-oxazolin-2-yl)-terminated oligopropene macromonomers and to investigate cationic bulk polymerization at elevated temperatures and polymer analoguous reaction with poly(ethene-co-methacrylic acid) containing 3mol% methacrylic acid to form novel graft copolymers via reactive processing technology.

Experimental

Materials: atactic mono(methylester)-terminated oligo(propene) of M_n=640 g/mol (vapor pressure osmometry) and M_n=790 g/mol with M_w/M_n=1.73, as determined by means of size exclusion chromatography (SEC), was supplied by BASF AG in Ludwigshafen. According to ^{1}H-NMR spectroscopic analysis, this product, prepared by carbonylation of vinylidene-terminated oligopropene, contains only 38mol% of the desired ester functionality. Byproducts are non-reacted vinylidene-terminated oligopropene and non-functional oligopropene resulting from hydrogenation which is encountered as side reaction during the carbonylation reaction.

Preparation of mono-N(2-hydroxyethyl-amide)-terminated-oligopropene(PP-CONHCH$_2$ CH$_2$OH): A mixture of 40.0 g (24 mmol) atactic methylester-terminated oligopropene and 2.9 g (48 mmol) 2-aminoethanol were heated for 24 h at 170 °C in the presence of 0.1 wt% phenolic antioxidant (Irganox®1010 from Ciba). During amide-formation methanol was distilled off. When the reaction was completed, the residual excess 2-ethanolamine was stripped off in oil pump vacuum and 41.5 g of viscous mono-N(2-hydroxyethyl-amide)-terminated oligopropene was recoverd. According to NMR analysis, no residual oxazoline was found. FTIR(film): 1600 cm^{-1}(C=O), 1559 cm^{-1} (NH), ^{1}H-NMR (300MHz, $CDCl_3$): δ=6.18 (s,NH, 1H); 4.98-4.68 (m, CH=); 3.72 (t, CH_2O, 2H); 3.44 (q, CH_2N, 2H); 2.52-0.68 (m, CH, CH_2, 200H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ=174.9 (CONH); 134.5-131.1 (C=C); 62.4(CH_2O); 47.6-43.3 ($\underline{CH_2}CH$); 42.4 ($\underline{CH_2}N$); 41.6-38.5 ($CH_3CH_2\underline{CH_2}$); 29.8 ($CH_3CH_2CH_2\underline{CH}$); 28.0-25.0 (CH); 24.2-18.0; 15.9-14.5 ppm(CH_3), M_n=660 g/mol (vapor pressure osmometry), M_n=800 g/mol and M_w/M_n=1.70 (SEC in chloroform solution).

Preparation of mono(1,3-oxazolin-2-yl)-terminated oligopropene (PP-OXA): 40 g of PP-$CONHCH_2CH_2OH$, containing 38 mol% N-(2-hydroxyethyl)amide endgroup, was heated together with 0.16g (0.48mmol) $Ti(On\text{-}C_4H_9)_4$, this corresponded to 2 mol% with respect to amide, at 180 °C under oil pump vacuum for the duration of 24 h to yield 39.4 g of a viscous oil where all amide groups were converted into oxazolines. For removal of vinylidene- and non-functional oligopropene the product was separated using a deactivated silica column (100 g silica was deactivated with 40g water) and toluene solvent. Yield of pure mono(1,3-oxazolin-2-yl)-terminated oligopropene was 14.2 g. Elemental analysis of $(C_3H_6)_{15}(C_3H_4NO)$ calc. (found), % C: 82.36 (82.09), % H: 13.54(13.66), % N 2.00(2.15); FTIR (film): 2965-2822 cm^{-1} (CH), 1668cm^{-1}(C=N), 1460 cm^{-1}, 1379cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ=4.14 (t, CH_2O, 2H); 3.75 (t, CH_2N, 2H); 2.29-1.81 (m, $\underline{CH}CH_2CN$, 3H); 1.50(m, CH, 13H); 1.32-0.62 ppm (m,$\underline{CH_2}$,CH_3,76H); ^{13}C-NMR(75MHz, $CDCl_3$): 168.0 (C=N), 67.0 (CH_2O); 54.3(CH_2N); 47.6-43.3($\underline{CH_2}CH$); 41.7-38.3 ($CH_3CH_2\underline{CH_2}$); 36.5-34.5 ($CH_3CH_2\,\underline{CH}$); 29.8 (CH_2-N); 28.5-26.6 (CH); 22.1-18.8 (CH_3); 14.2 ($\underline{CH_3}CH_2CH_2$), M_n=660g/mol (vapor pressure osmometry), M_n=830g/mol and M_w/M_n=1.62 (SEC in chloroform), M_n=710 g/mol as determined by endgroup titration (0.1N $HClO_4/CH_3COOH$, solution in $CH_3COOH/CHCl_3$=1:1), T_g=-54.3 °C determined by means of DSC.

Preparation of poly[N-oligopropene-1-carbonyl-ethyleneimine] (PP-PEI): A mixture of 1.00 g (1.43 mmol) PP-OXA and 6.3 mg (0.029 mmol) methyl-4-nitrobenzenesulfonate were heated 10 min at 200 °C. Viscosity build-up was accompanied by disappearance of ^{1}H-NMR signals typical for the oxazoline group. The resulting PP-PEI was dissolved in chloroform and extracted with diluted aqueous $NaHCO_3$ to remove initiator. After drying over $MgSO_4$, solvent was stripped off and PP-PEI was dried at 60°C in oilpump vacuum to afford 0.96 g (96%) of a slightly yellow viscous oil. Elemental analysis of $[(C_3H_6)_{15}(C_3H_4NO)]_x$ calc. (found): % C 82.36 (82.48), % H 13.54 (13.29), % N 2.00 (2.05); FTIR(film): 2967-2820cm^{-1} (NH), 1650cm^{-1} (C=O), 1460 cm^{-1}, 1379 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ=3.38(s, CH_2N, 4H); 2.29-1.90 (m, $CHCH_2CO$, 3H); 1.50 (s, CH, 13H); 1.31-0.62 ppm (m, CH_2,CH_3,76H); ^{13}C-NMR(75 MHz, $CDCl_3$): δ=174.5-172.0 (CO); 47.4-43.2 ($\underline{CH_2}CH$); 41.5-38.4 ($\underline{CH_3}CH_2CH_2$, CH_2N); 29.6 ($CH_3CH_2CH_2CH$); 27.2 (CH); 22.0-18.6 (CH_3); 14.4ppm ($\underline{CH_3}CH_2CH_2$); M_n=22100 g/mol and M_w/M_n=2.2 (SEC in $CHCl_3$), Tg=-27.8 °C, as measured by means of DSC.

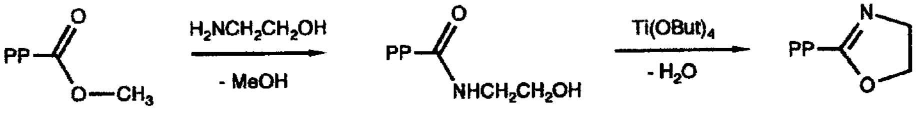
Melt grafting: A mixture of 2.00 g poly(ethene-co-methacrylic acid), containing 3mol% (equivalent to 2.02 mmol) methacrylic acid, 1.41g (2.02mmol) PP-OXA and 3.4mg(0.1wt%) Irganox® 1010 were heated at 220 °C for the duration of 15 min to obtain a homogeneous melt. The resulting polymer was dissolved in $CHCl_3$ and precipitated in excess Et_2O which is a solvent for PP-OXA. After drying at 60°C under oilpump vacuum, 3.27 g (96 %) of a white polymer was obtained. Elemental analysis of $(C_2H_4)_{32}[C_7H_{10}NO_3(C_3H_6)_{15}]$ calc.(found): % C 82.68 (82.33), % H 13.64 (13.88), % N 0.83 (0.99); FTIR (film): 3290cm^{-1} (NH), 2918 cm^{-1}, 2849 cm^{-1} (CH), 1730 cm^{-1} (C=O), 1645 cm-1 (NHC=O), 1540 cm-1(NH), 1463 cm^{-1}, 1379 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.62 (s, NH, 1H); 4.09(s, CH_2O, 2H); 3.44 (s, CH_2N, 2H); 2.09 (s, $\underline{CHCH_2}CONH$,3H), 1.70-0.55 ppm (m, CH, CH_2, CH_3, 220H), T_g=-20.9 °C, T_m=95.1 °C, ΔH= -43.0 J/g (determined by means of DSC), and Tg=-18.4 °C, as measured with DMA using 5 $Kmin^{-1}$ heating rate.

Characterization: NMR studies were performed on a Bruker AMR 300 spectrometer. FTIR spectra were recorded using a Bruker IFS 88 spectrometer. For measurement of elemental analyses a Perkin Elmer Elemental Analyzer 240C was used. Molecular weight distributions were measured by means of size exclusion chromatography equipped with Styragel columns using polystyrene calibration. For molecular weight measurement also vapor pressure osmometry (Perkin Elmer Molecular Weight Apparatus Type 115) at 30 °C was applied. Thermal properties and phase transition were determined using DSC (Perkin Elmer DSC-7, heating rates of 9, 16, 26, 36 $Kmin^{-1}$ and extrapolation to 0 $Kmin^{-1}$) and dynamic mechanical analysis (Rheometrics Solids Analyzer RSA II) with 50x6x2 mm double cantilever test specimen, 1 Hz, 2-5 $Kmin^{-1}$ heating rate and amplitude of 0.3 %.

Results and Discussion

The non-stereoselective methylalumoxane-activated Cp_2ZrCl_2 catalyst polymerizes propene to produce atactic vinylidene-terminated oligopropene which is converted into monomethylester-terminated oligopropene via carbonylation reaction. Such monoester-terminated oligopropenes, e.g., atactic monomethylester-terminated oligopropene with molecular mass of M_n=640 g/mol and approximately 15 propene repeat units, are appropriate starting materials for oxazoline synthesis. According to Scheme 1, similar to synthetic procedures developed for the production of 2-substituted 1,3-oxazolines derived from fatty acid esters [10], monomethylester-terminated oligopropene reacts with two-fold molar excess of 2-aminoethanol at 170°C to convert the ester endgroup into the corresponding N-(2-

hydroxyethyl)-amide. As demonstrated by ^{1}H-and ^{13}C-NMR-analysis, no side reactions take place and the amide is obtained in essentially quantitive yield. After removing excess reagent, heating the amide at 180°C and stripping off water in vacuum yields mono(1,3-oxazolin-2-yl)-terminated oligopropene as viscous oil with glass temperature of Tg=-54.3 °C. Preferably this thermal cyclization reaction is catalyzed by addition of 2 mol% $Ti(OC_4H_9)_4$ with respect to the amide. Again this reaction sequence can be monitored by means of ^{1}H-NMR spectroscopy which confirms quantitative amide conversion. In the ^{1}H-NMR spectrum, the signals at 3.72 ppm (t, $-CH_2O$) and 3.44 ppm(t,$-CH_2N$) disappear, whereas new signals at 4.14 ppm (t,$-CH_2O$) and at 3.75 ppm (t, CH_2N) correspond to the two methylene groups of the 1,3-oxazoline ring.



Scheme 1

PP-OXA

Since the monoester-terminated oligopropene contains 62mol-% impurities such as residual vinylidene-terminated and hydrogenated oligo(propene) as byproducts of the carbonylation reaction, silica-column-chromatography has been applied successfully to purify the oxazoline macromonomer. In order to avoid decomposition of the oxazoline during chromatographic separation, silica must be deactivated by adding water before charging the oxazoline. The ^{13}C-NMR spectrum of the oxazoline macromonomer is displayed in Fig.1.

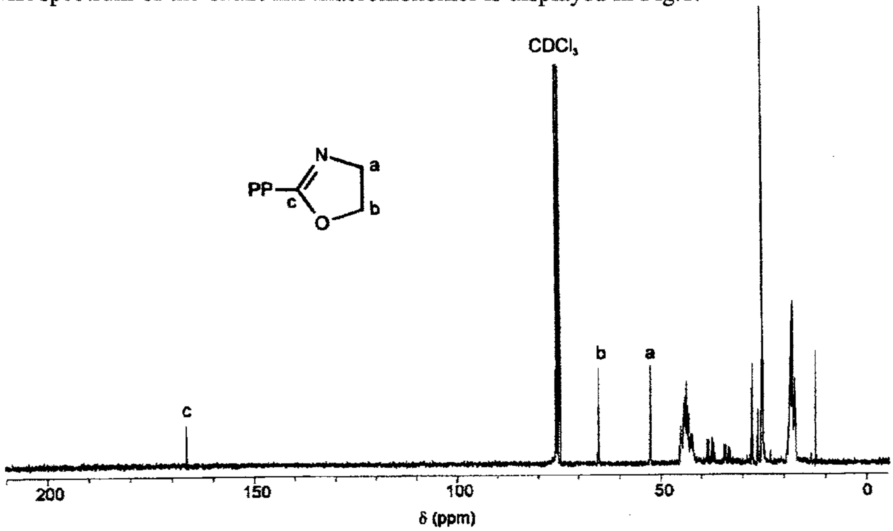


Fig.1 ^{13}C-NMR spectrum (75 MHz) of PP-OXA in $CDCl_3$.

Cationic polymerization of PP-OXA was initiated by adding methyl-4-nitrobenzenesulfonate as initiator, thus methylating oxazoline ring to form the corresponding oxazolinium ion which is an effective initiator at elevated temperature. In fact, upon heating 10 minutes at 200°C the NMR signals typical for the methylene groups disappear. According to ^{1}H- and ^{13}C-NMR analyses, the resulting polymer is a poly[N-oligopropene-1-carbonyl-ethyleneimine], abbreviated as PP-PEI, which is amorphous and exhibits a glass transition at -27.8 °C. Shown in

Fig.2 is the ^{13}C-NMR spectrum of PP-PEI. According to size exclusion chromatography (SEC), the molecular mass of M_n=22100 g/mol, measured by using polystyrene-based SEC calibration, is in acceptable agreement with the theoretical M_n=35000 g/mol, expected on the basis of the PP-OXA/initiator molar ratio of 50 mol/mol. Moreover, the surprisingly narrow polydispersity of M_w/M_n=2,2 demonstrates that controlled cationic polymerization takes place at 200°C within a few minutes.

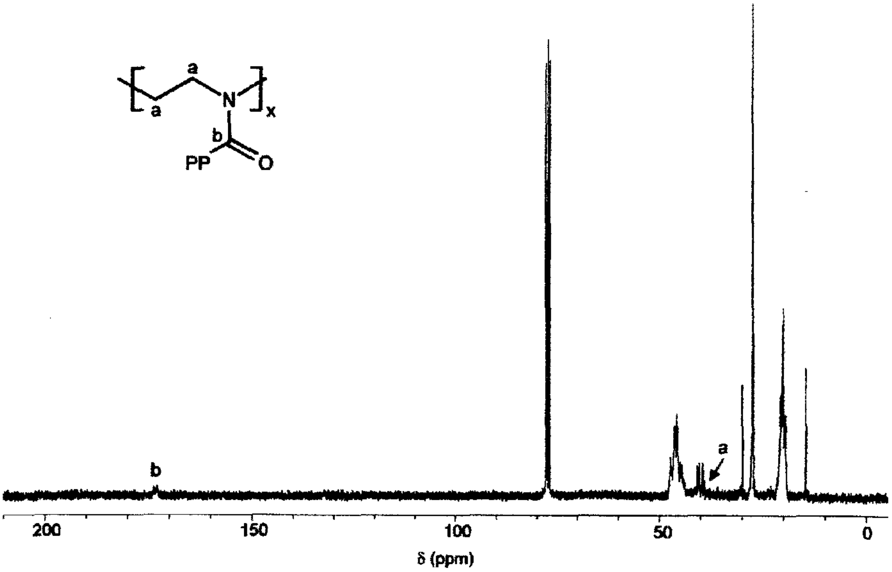
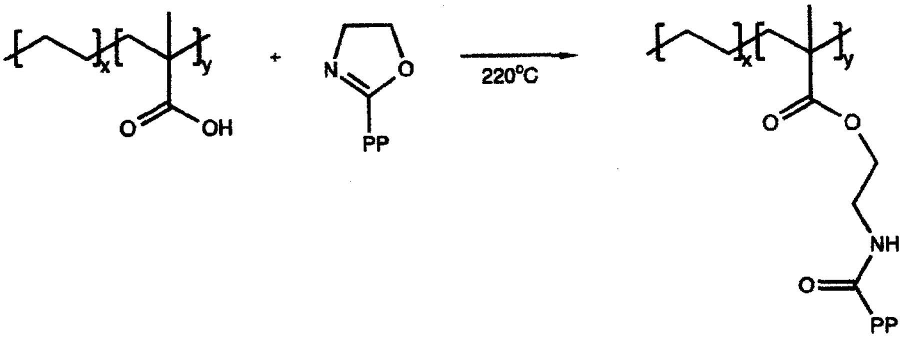


Fig.2 ^{13}C-NMR (75 MHz) spectrum of PP-PEI in $CDCl_3$.

In addition to cationic ring-opening polymerization, 2-substituted 1,3-oxazoline can also undergo ring-opening as a result of nucleophilic attack at C-5 of the oxazoline ring. Recently, this reaction has been applied by Müller et al. [11] to diversify poly(ethene-co-methacrylic acid) which reacts with 2-substituted 1,3-oxazolines to produce a wide range of ethene copolymers with esteramide side chains. Similarly, as shown in Scheme 2, PP-OXA reacts with poly(ethene-co-methacrylic acid) to form novel ethene copolymers containing esteramide-coupled oligopropene side chains.

Esteramide-coupling reaction is achieved by heating poly(ethene-co-methacrylic acid), containing 3 mol% methacrylic acid, together with stoichiometric amount of PP-OXA within a few minutes at 220 °C. Although both components are initially immiscible, after a few minutes a homogeneous polymer melt is formed. According to FTIR analysis, the absorption at 2750-2300 cm-1 and at 1700 cm-1, which are typical for carboxylic acids, disappear while simultaneous appearance of new IR absorptions at 3290, 1730, 1645 and 1540 cm-1 reflect formation of esteramide moities. Also esteramide coupling is a high yield reaction without any detectable side product formation.



Scheme 2

In contrast to poly(ethene-co-methacrylic acid), the esteramide derivative is very well soluble in chloroform The resulting esteramide-functional ethene copolymer is dissolved in chloroform and precipitated in diethyl ether, which is a good solvent of PP-OXA. In spite of 41 wt% PP-OXA addition, neither residual PP-OXA nor other oligopropenes are extracted. This again represents experimental evidence supporting the spectroscopic determination of complete PP-OXA conversion. When 41 wt-% PP-OXA are coupled onto poly(ethene-co-methacrylic acid), melting temperature is lowered from 100 to 95°C, heat of fusion of the oligoethene segments from 59.5 to 43.0J/g, whereas glass temperature decreases from 25°C to -21°C. This behavior is shown by the dynamic mechanical analysis of the two polymers, which is displayed in Fig.3. The substantially lower glass transition is typical for that of the oligopropene side chain. As a consequence, the thermoplastic poly(ethene-co-methacrlyic acid) is converted into a rubbery polyethene-*graft*-oligopropene.

Conclusion

Mono(1,3-oxazolin-2-yl)-terminated oligo(propenes) are highly reactive and selective intermediates which can be used as macromonomers to produce N-acylated poly(ethyleneimines) conatining oligopropene side chains. Moreover, as a result of the facile ring-opening substitution, such reactive intermediates can be used to attach oligo- and polypropene segments to various polymer chains, especially to polymer endgroups. This represents an attractive route to AB- and ABA-type segmented polypropenes, which are of interest as compatibilizers in polymer blends and components of adhesives. The same concept can be applied to modify other olefin polymers which are readily available via metallocene-catalyzed polymerization.

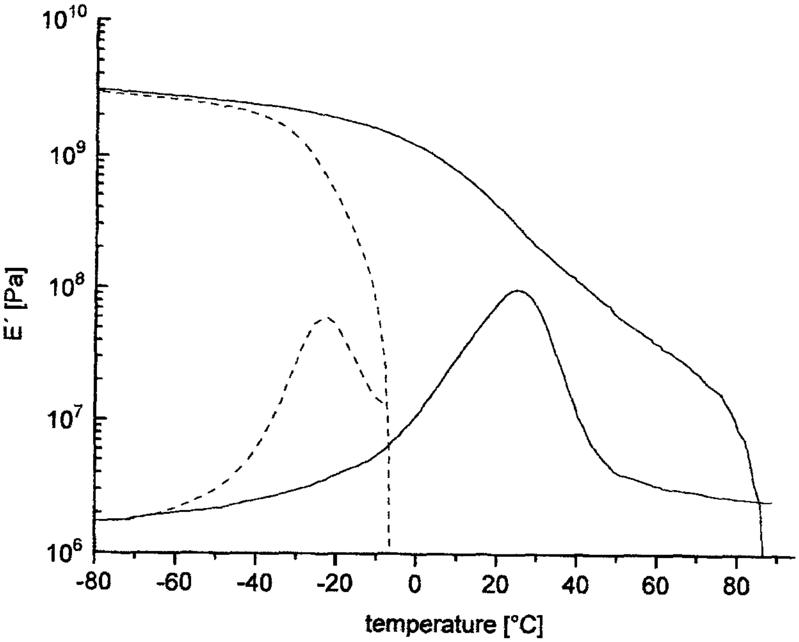


Fig.3 Dynamic mechanical analysis of poly(ethene-co-methacrylic acid) (solid line) and polyethene-*graft*-oligopropene (dotted line).

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