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The synthesis of polyepoxides from unsaturated polymers and their attempted isomerisation to polyketones

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Polybutadienes or polyisoprenes with $>98\%$ *E*-double bonds in the backbone can be epoxidised in quantitative yield to polyepoxides using Bu^tOOH in the presence of dichloro[(1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor]dioxomolybdenum(VI) and molecular sieves. The polymers formed can be isolated in a pure form provided that HCl, which otherwise promotes crosslinking, is removed from the reaction solution.

Attempts to isomerise the polyepoxides to polyketones using LiBr in the presence or absence of hexamethylphosphoramide (HMPA) or dimethylimidazolidinone (DMI) were partially successful, although the products generally tended to be insoluble as a result of aldol-type crosslinking reactions. For epoxides derived from polyisoprene, soluble isomerisation products can be obtained but these contain, in addition to ketone and unreacted epoxide units, ketals formed from reactions of isomerising epoxides with adjacent intact epoxide units.

The thermal properties of the polyepoxides are discussed.

Polymers containing epoxide groups have significant uses in the coatings and adhesives industries and are of two main types. Prepolymers to epoxy resins[1] contain both terminal epoxy groups and hydroxy groups pendant from the main chain. They are formed by the reaction of a diol with, for example, chloromethylethene oxide. Ring opening of the epoxide gives a chlorohydrin, with a remote hydroxy group. A new epoxide unit is formed from the chlorohydrin by treatment with base. The density of epoxide linkages in these polymers is generally low. Crosslinking is then effected by intermolecular ring opening of the epoxide ring by the pendant hydroxy groups. The other type of epoxide, which has much higher loadings of epoxy rings, is formed by the stoichiometric (using peracids)[2,3] or catalytic[4,5] epoxidation of unsaturated polymers. During the course of studies aimed at the selective functionalisation of the different kinds of double bonds in polybutadienes[5–9] which contain both backbone and pendant double bonds, we investigated the epoxidation of these polymers using Bu^tOOH and [MoO_2Cl_2L] [L = 3-(diethoxyphosphoryl)-camphor][10–12] and found that this showed very high selectivity for the functionalisation of the backbone double bonds over the pendant double bonds. Small amounts of diol were also formed but these could be reduced if the reaction was carried out in the presence of molecular sieves.[5*b*,*c*] In that study, we reported on the epoxidation of a polybutadiene containing $>98\%$ backbone double bonds in which we obtained up to 85% conversion of the double bonds to epoxide groups.[5*b*,*c*]

Because of the commercial potential of these highly epoxidised polymers and because they might be capable of further chemical modification, we have now carried out an indepth study of the epoxidation of polybutadienes as well as of polyisoprene. We have also studied the isomerisation of the polyepoxides to polyketones.

Experimental

Atomic absorption analyses and microanalyses were performed at the University of St. Andrews. Solution phase NMR spectra were recorded on a Brüker AM300 spectrometer operating in the Fourier transform mode with, for ^{13}C, broadband proton decoupling, solid state NMR spectra on a Brüker MSL 500 using magic angle spinning and cross-polarisation, IR spectra on a Perkin-Elmer PE 1710 FTIR spectrometer and thermal analyses on a TA Instruments SDT 2960 simultaneous thermal analyser over the temperature range 25–400 °C with a heating rate of $10\,^{\circ}C\ min^{-1}$.

Polybutadienes were obtained from Aldrich [M_w $(2–3)\times10^6$] or Scientific Polymer Products [M_w $(2–3)\times10^5$] and polyisoprene (product 18.214-1) from Aldrich. All polymers had $>98\%$ *cis*-1,4 units as confirmed by ^1H and ^{13}C NMR spectroscopy.[8] LiBr (Aldrich) was dried before use by pumping *in vacuo*, whilst hexamethylphosphoramide (HMPA, Aldrich), *tert*-butyl hydroperoxide (TBHP, $3.0\ mol\ dm^{-3}$ in 2,2,4-trimethylpentane, Fluka) and dimethylimidazolidinone (DMI, Aldrich) were used without purification. The complex, dichloro[(1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor]dioxomolybdenum(VI) (MoO_2Cl_2L) was prepared by a standard literature method.[10] Molecular sieves (4 Å, activated powder, average particle size 2–3 µm, Aldrich) were predried as described below.

All manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk-line and catheter tubing techniques. Solvents were dried by distillation from sodium diphenyl ketyl (toluene, THF, diethyl ether), sodium (light petroleum, boiling range 40–60 °C) or calcium hydride (CH_2Cl_2). Benzene (May and Baker) was used as received.

Synthesis of epoxides

(a) In the presence of molecular sieves.[11,12] Molecular sieves (4 Å, 10 g) were heated *in vacuo* for 5 min. A solution containing polybutadiene (0.54 g) or polyisoprene (0.68 g, 10 mmol of double bonds) in CH_2Cl_2 or THF ($40\ cm^3$) was added followed by *tert*-butyl hydroperoxide (1.25 g, 13.89 mmol in 2,2,4-trimethylpentane). After stirring for 30 min and optionally cooling to 0 °C, [$MoO_2Cl_2L_2$] (0.1 g, 0.21 mmol) in CH_2Cl_2 or THF ($10\ cm^3$) was added and the resulting suspension was stirred for 18 h at room temperature.

(b) In the absence of molecular sieves.[12] These reactions were carried out as in (*a*), above, but omitting the molecular sieves.

(c) Using a preformed MoO_2–molecular sieves complex. Molecular sieves (4 Å, 10 g) were heated *in vacuo* for 5 min. [$MoO_2Cl_2L_2$] (0.1 g, 0.21 mmol) in CH_2Cl_2 or THF ($10\ cm^3$) was added and the resulting suspension was stirred for 15 min.

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After the molecular sieves had settled, the solution was decanted and replaced by a solution containing polybutadiene (0.54 g) or polyisoprene (0.68 g, 10 mmol of double bonds) in CH_2Cl_2 or THF (40 cm^3). After stirring for 15 min, *tert*-butyl hydroperoxide (1.25 g, 13.89 mmol in 2,2,4-trimethylpentane) was added and the solution allowed to stir for 24 h at room temperature. Similar high conversions of the double bonds were obtained using a stoichiometric amount of *tert*-butyl hydroperoxide.

Purification of polyepoxides

The product solutions obtained as described above were allowed to settle and the bulk of the molecular sieves removed by filtration. They were then centrifuged to settle the last traces of molecular sieves, decanted and stirred with $CaCO_3$ (0.45 g, 0.42 mmol) for 30 min to remove any HCl produced during the reaction. The mixture was again centrifuged and decanted into light petroleum (100 cm^3). The polymer that separated was collected and dried *in vacuo*. Epoxide from polybutadiene: Found C 65.9, H 8.2; $[C_4H_6O]_n$ requires C 68.6, H 8.5%. Epoxide from polyisoprene: Found C 68.8, H 8.8; $[C_5H_8O]_n$ requires C 71.4, H 9.5%. The Mo content of the purified polymers formed by method (*c*) were 0.8 and 1.2% respectively. NMR: epoxidised polybutadiene, δ_H(all broad singlets) 1.7 (1H), 1.8 (2 H) and 1.9 (1H) (all CH_2), 3.0 (2 H) (CH). δ_C 25.1 and 25.3 (CH_2), 56.6 and 56.9 (CH); epoxidised polyisoprene, δ_H (all broad singlets) 1.3 (3 H) (CH_3), 1.7 (2 H) and 1.8 (2H) (both CH_2), 2.8 (1 H) (CH). δ_C 23.0 (CH_3), 26.0 and 31.0 (CH_2), 60 8 and 60.6 (CMe), 64.4 and 64.6 (CH).

Isomerisation of polyepoxide

(a) HMPA as solubiliser.[13] (i) HMPA (0.45 g, 2.5 mmol) was added to a stirred solution of epoxidised polybutadiene (0.7 g, 10 mmol of epoxide) or epoxidised polyisoprene (0.84 g, 10 mmol of epoxide) in benzene, CH_2Cl_2, or THF (50 cm^3). The solution was refluxed for 15 min and cooled to room temperature. LiBr (0.2 g, 2.5 mmol) was added and the solution stirred for 10 min. Part of this solution (1 cm^3) was transferred into an NMR tube, where it was partially evaporated and $CDCl_3$ added. Any solid product in the initial solution was collected by filtration and analysed by IR and solid state NMR spectroscopy.

(ii) A solution of polybutadiene epoxide (0.7 g, 10 mmol) or polyisoprene epoxide (0.84 g, 10 mmol) in benzene, CH_2Cl_2, or THF was treated with a solution of LiBr (0.4 g, 5 mmol) and HMPA (0.9 g, 5 mmol) in benzene, CH_2Cl_2 or THF (30 cm^3). The resulting mixture was refluxed for 15 min, cooled and washed with water. The organic layer was decanted and evaporated to dryness to give, in the case of polybutadiene epoxide, only a small amount of residue. Examination of the residue by IR spectroscopy showed only $\nu_{C=O}$ from the free β-keto phosphonate ligand (1740 cm^{-1}) in the carbonyl stretching region. The main bulk of the product was a rubbery solid adhering to the sides of the initial reaction vessel. This was separated from the water washings, dried *in vacuo* and analysed by IR spectroscopy. For polyisoprene epoxide, part of the organic layer was decanted into an NMR tube and treated as described in (*a*) (i) above. γ-Butyrolactone, identified by its ^1H NMR spectrum, was observed as a product in reactions starting from epoxidised polybutadienes carried out in THF.

(iii) Polybutadiene epoxide (0.7 g, 10 mmol) or polyisoprene epoxide (0.84 g, 10 mmol), LiBr (0.5 g, 5.7 mmol) and HMPA (1.0 g, 5.7 mmol) were dissolved in benzene, CH_2Cl_2 or THF (50 cm^3). The resulting mixture was then refluxed for 15 min, cooled and worked up as in (ii) above. A sample of a polymer prepared in this way from polybutadiene epoxide was analysed by solid state (CPMAS) ^{13}C NMR spectroscopy. δ_C 21, 23, 39 and 44 (CH_2), 130 ($CH{=}CH$), 210 ($C{=}O$).

(iv) As in (*a*)(ii) above, but using varying amounts of LiBr and HMPA.

Methods (*a*)(i) and (*a*)(ii) were also attempted using 2,3-epoxybutane (0.5 g) in place of the polymeric epoxide; only method (*a*)(ii) produced butan-2-one (95% yield by ^1H NMR analysis in 3 h, 40% in 1 h).

(b) DMI as solubiliser. (i) As in (*a*)(i) above, but using DMI (0.45 g, 2.5 mmol) in place of HMPA.

(ii) As in (*a*)(ii) above, but using DMI (0.9 g, 5 mmol) in place of HMPA. After refluxing and cooling, the solution was analysed as in (*a*)(i) above. γ-Butyrolactone, identified by its ^1H NMR spectrum, was observed as a product in reactions starting from epoxidised polybutadienes carried out in THF.

Methods (*b*)(i) and (*b*)(ii) were also attempted using 2,3-epoxybutane (0.5 g) in place of the polymeric epoxide. Method (*b*)(ii) produced butan-2-one (>95% in 1 h).

(c) In the absence of solubiliser. As in (*b*)(ii) above in THF, except that solid LiBr was added in place of the solution containing LiBr and DMI. ^{13}C NMR: product from epoxidised polybutadiene: δ_C 56.6 and 56.9 (epoxide CH), 100, 105, 106, 108 (OCO, tentative assignment) 128, 130 and 131 ($CH{=}CH$), 203 ($C{=}O$); product from epoxidised polyisoprene (a soluble product was obtained from all reactions using HMPA or DMI in CH_2Cl_2 or no solubiliser in THF carried out by method (*b*)(ii), these all gave very similar resonances for the polymer C atoms), δ_C 60.6 and 60.8 (epoxide CMe), 64.4 and 64.6 (epoxide CH), 100, 104 and 105 (OCO), 203 and 204 ($C{=}O$); resonances from other C atoms are present in the aliphatic region of the spectrum, but the complicated microstructure of the polymer makes them difficult to assign with confidence.

Results and Discussion

Epoxidation reactions

The results of epoxidation reactions of the polydienes are collected in Table 1. In all cases complete conversion of the double bonds can be obtained, as indicated by the absence of characteristic peaks from the double bonds in the ^1H (δ 5.5) and ^{13}C (δ 130) NMR spectra. The best conditions for the epoxidation reactions (>95% conversion and >95% selectivity to the epoxide, even when using a stoichiometric amount of oxidant) involve loading the catalyst onto the molecular sieves (we have shown that both the β-keto phosphonate ligand and HCl are liberated in this step).[12] The molybdenum-containing molecular sieves are then separated from the liquid phase by filtration before addition of the reaction solvent (CH_2Cl_2 or THF), substrate and oxidant. After the reaction, the solutions are filtered,‡ stirred with solid $CaCO_3$ to remove any HCl present and the polymers precipitated by decanting into light petroleum as white rubbery powders, readily soluble in CH_2Cl_2 (polybutadiene) or THF (polyisoprene). Failure to remove the HCl leads to crosslinking ring-opening reactions such that the product polymers are difficult to redissolve in CH_2Cl_2 or THF. The reactions can also be carried out using a different reaction sequence, in which the molybdenum catalyst is added to a solution of the substrate, oxidant and molecular sieves, followed by a similar work-up procedure. The main disadvantage of this protocol is that more molybdenum is present in the final polymer. For reactions carried out in the absence of molecular sieves, small amounts of diol residues are obtained (δ_H 4.0, δ_C 83) presumably from ring-opening reactions with water catalysed by the Mo complex. We have shown separately that this catalyst is active, if rather slow, for such ring-opening reactions.[14]

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‡For the very high molecular weight polybutadiene (2–3 MD), the viscosity of the solution is such that the molecular sieves can be difficult to remove.

Table 1 Microstructure of polymers obtained by epoxidation of unsaturated polymers in CH_2CI_2 under a variety of conditions

substrate[a]	M_W/amu	catalyst[b]	epoxide units (%)	diol units (%)	unreacted double bonds (%)
PBD	$(2–3)\times10^6$	A	86	5	8
PBD	$(2–3)\times10^6$	B	>95	—	—
PBD	$(2–3)\times10^5$	A[c]	80	20	—
PBD	$(2–3)\times10^5$	B	>95	—	—
PBD	$(2–3)\times10^5$	C	>95	—	—
PISOP		A	70	30	—
PISOP		B	>95	—	—
PISOP		C	>95	—	—

[a]PBD is *cis*-polybutadiene, PISOP is *cis*-polyisoprene. [b]A = $[MoO_2Cl_2L]$, B = $[MoO_2Cl_2L]$ in the presence of molecular sieves, C = MoO_2 supported on molecular sieves. [c]Catalyst concentration is double that usually employed.

Spectroscopic properties of the epoxide polymers

^1H and ^{13}C NMR analysis of the purified polymers shows that only resonances characteristic of the polyepoxide are present, with no evidence for unreacted double bonds or diol formation. Of particular interest is the observation that the ^{13}C NMR resonance of each non-equivalent epoxide C atom in epoxidized polybutadienes appears as two peaks of equal intensity. We assign these as arising from the random orientation of the epoxide oxygen atoms at either side of the chain. One resonance arises from C atoms for which the O atom of the next unit is on the same side of the chain as that in the epoxide of the C atom in question, whilst the second resonance is from C atoms where the next O atom is on the opposite side of the chain (Fig. 1). This random orientation also gives rise to non-equivalences in the CH_2 protons of the chain, which resonate as a broad triplet. Examination of the structure of the polymer (Fig. 1) shows that, in the conformation shown, the H atoms of each methylene unit are inequivalent but the H atoms of pairs of methylene groups are related by a local centre of inversion (CH_AH_B) or a local two-fold axis perpendicular to the plane of the polymer backbone (CH_CH_D) (assuming that the environment of the H atoms is only affected by the epoxide groups on each side of the methylene group in question). It seems probable then that the highest field signal is from H_D (on the opposite side of the chain from both adjacent epoxide O atoms) and the lowest field is from H_C (on the same side as both adjacent O atoms). The resonances from H_A and H_B then overlap since they have one adjacent O atom on the same side of the chain and the other on the opposite side.

For the epoxidised polyisoprene, the two carbon atoms of the double bond are non-equivalent and give rise to resonances near δ 61 (CCH_3) and 64 (CH), with both appearing as double peaks because of the random orientation of the epoxide linkages along the chain. This random orientation ensures that there are eight different H environments for the methylene protons, but these appear as two broad resonances near δ 1.75. The CH_2 carbon atoms resonate as two singlets at δ 26 and 31. The epoxide protons resonate as a broad singlet, despite the fact that the O atom of the next epoxide in the chain can be on the same side or the opposite side of the chain relative to these protons. This suggests that the chemical shift of this proton is relatively insensitive to the stereochemistry of the C atom in the δ position. The methyl resonances of the isoprene units appear as a singlet at δ 23 in the ^{13}C NMR and a broad singlet at δ 1.3 (^1H).

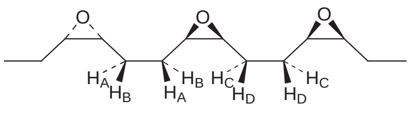

Fig. 1 Structure of polybutadiene epoxide showing the various types of H atom present

Physical and thermal properties of polyepoxides

The polyepoxides are all white rubbery powders which redissolve in CH_2Cl_2 or THF provided they have been purified to remove HCl. In general, they contain appreciable amounts of Mo from the catalysts (up to 75% of that used) but the amount of Mo can be greatly reduced by using the preformed Mo–molecular sieves catalyst (see Experimental).

In the STA (Table 2), the polymers all show a small weight loss below 100 °C which we attribute to loss of entrapped solvent. There is then a fairly sharp exotherm peaking above 200 °C. Since this is not accompanied by a weight loss, we assume this corresponds to an isomerisation of the epoxide, probably to a polyketone. There is then a weak endotherm below 300 °C which is accompanied by weight loss. We attribute this to crosslinking of the polyketones by aldol condensation with the weight loss being caused by loss of water. Finally, there is a more substantial endothermic weight loss above 300 °C presumably arising from complete polymer degradation.

Attempted ring-opening reactions

The importance of polyketones as photodegradable polymers[15] and structural materials led us to investigate the isomerisation of polyepoxides by ring-opening isomerisation to form polyketones. One of the most important polyketones is that derived from the alternating copolymerisation of carbon monoxide and ethene. This polymer has excellent properties in film form, but the regularity of its structure means that it has crystalline domains which lead to a high melting point, which is close to its decomposition temperature. This, in turn, means that there are problems with processing the polymer. Generally, these are improved by adding propene to the feedstock so as to introduce some irregularity into the chain and lower the melting point. This polymer has just been commercialised[16] for such uses as blades for lawn mowers or gear wheels.

In their backbones, these polymers contain two C atoms between each C=O unit, and we reasoned that further advantages in terms of processing might be possible if either this chain length were variable (2,3 or 4 C atoms between C=O units) or it were longer, increasing rotational degrees of freedom by having fewer sp^2 hybridised C atoms.

In principle, isomerisation of the polyepoxides in the epoxidised polybutadienes or polyisoprenes should be able to provide polyketones of this type (see Fig. 2). Related polymers have been synthesised before by the direct oxidation of polybutadienes, but in all cases, the starting materials have contained pendant double bonds which oxidise preferentially to the backbone double bonds to give pendant methyl ketone units.[4,17] Oxidation of the backbone double bonds can also be achieved; however, the yields are low.[4] Several catalysts are available for isomerisation of epoxides to ketones but one of the most effective involves a 1 : 1 mixture of LiBr and hexamethylphosphoramide (HMPA) in benzene.[13] We have studied

Table 2 Simultaneous thermal analysis (STA) data for polyepoxides[a]

T_{onset}/°C			weight loss (%)			theoretical weight loss	
PBDO	PISOPO	ΔH^b	PBDO	PISOPO	assignment	PBDO	PISOPO
50	50	+	5	10	Solvent loss		
175	180	−	0	0	Isomerisation		
260	230	+	15	10	Crosslinking	12.8	10.7
360	280	+	61	75	Decomposition		

[a]PBDO is purified polybutadiene epoxide, PISOPO is purified polyisoprene epoxide. [b]+ is endotherm, − is exotherm.

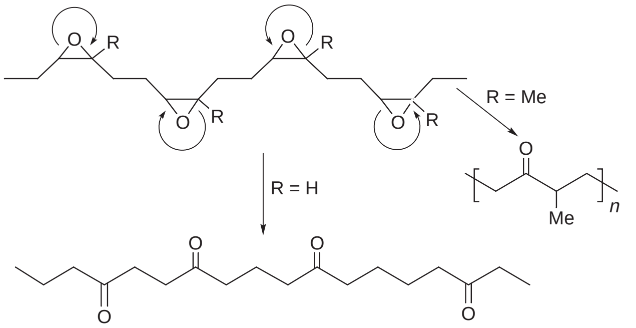

Fig. 2 Ring opening of polyepoxides showing the random microstructure that can in principle be obtained from polybutadiene (R = H), or the methyl substituted polymer that can be obtained from polyisoprene (R = Me). The arrows on the epoxide indicate the direction of opening of the epoxide in the polybutadiene epoxide. The ring openings are accompanied by a H shift.

this system for the isomerisation of the epoxidised polymers and find that, for the polybutadiene epoxides, white solids which are insoluble in all common organic solvents, including *m*-cresol and perfluoroisopropyl alcohol are obtained. These solids all show a band at 1710 cm^{-1} in their infra-red spectra and a solid state ^{13}C NMR spectrum of one of the samples (Fig. 3) showed a strong resonance at δ 210. Both of these indicate that ketone functions are formed, and the absence of peaks near 905 and 965 cm^{-1} in the IR spectra or δ 55 in the solid state ^{13}C NMR spectrum indicate that little or no epoxide groups remain. Surprisingly, the solid state ^{13}C NMR spectrum contains a resonance near δ 130, suggesting that there is a substantial amount of double bonds in the final polymer. This suggests that the polymer may have undergone crosslinking *via* an aldol condensation reaction. This, in addition to the high initial molecular weight of the polymer, may perhaps account for the low solubility of the product. We have also shown that very similar products are obtained if the reaction is carried out using DMI in place of HMPA in either CH_2Cl_2 or THF. The role of the HMPA or DMI is to solubilise the LiBr in an organic solvent, but since LiBr dissolves in THF without a solubilising agent, we find that the same reaction to give a very similar product also occurs if the reaction is carried out in THF in the absence of a solubilising agent. In this case, it is possible to obtain a product which is partially soluble in THF. The ^{13}C NMR spectrum for this polymer shows a resonance at δ 203 characteristic of ketone units, showing that the isomerisation has been successful, but the conversion is low, as indicated by the presence of resonances from the epoxide C atoms near δ 57 and a resonance near δ 130 is consistent with some aldol-type crosslinking having occurred.

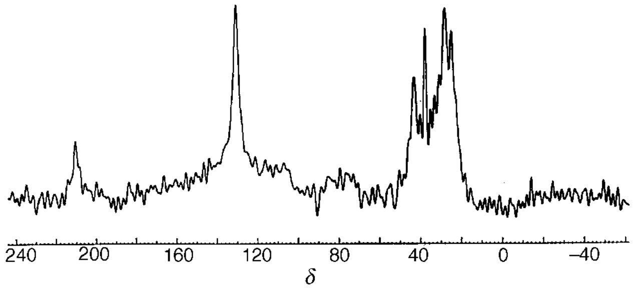

Fig. 3 Solid state CPMAS ^{13}C NMR spectrum of a polyketone prepared by isomerisation of an epoxidised polybutadiene [$M_w = (2–3) \times 10^6$] using LiBr–HMPA

Using epoxidised polyisoprene as the substrate, a soluble product can be obtained by using HMPA or DMI in CH_2Cl_2 or THF or by using LiBr alone in THF. ^{13}C NMR studies of the crude reaction solution show the presence of two resonances at δ 203 and 204, characteristic of ketone units, although not all of the epoxide units have ring-opened as indicated by residual resonances at δ 60.6, 60.8, 66.4 and 66.6. In addition, there are four very intense resonances near δ 100, in the region in which acetal or ketal carbon atoms resonate. Although some of these resonances may be associated with products obtained from ring-opening or oxidation of THF (γ-butyrolactone is also a product), others are clearly associated with the polymer. We assign them as arising from a reaction between ketone units and neighbouring epoxides to give brevicomin[18,19] type structures along the polymer chain (Fig. 4). These type of bicyclic ketals readily form from epoxy ketones where the ketone is separated from the epoxide by two or three sp^3 carbon atoms. Ketals of a different kind can also be formed during the synthesis of CO–alkene copolymers, especially if the alkene contains an α-substituent, but the regular arrangement of C=O groups along the chain ensures that these are monocyclic and that all the ketonic groups form ketals.[20–22] In these polymers, resonances from the ketal carbon atoms appear at δ 113 in the ^{13}C NMR spectrum.[21]

The opening of the epoxides presumably occurs in a random fashion along the polymer chain and the brevicomin type units can only occur when a ketone, or the alkoxide intermediate, is formed on the unit next to an intact epoxide. In the early stages of the reaction, this will normally be the case, but later on, the random nature of the reaction means that some epoxide units will become isolated between brevicomin units. These will either oxidise to isolated ketone units, which will remain as ketones, or may be too sterically hindered to be attacked. This perhaps accounts for the fact that very high conversions have not been observed and that the resonances from the brevicomin type units are the major product resonances. The fact that all the resonances are multiple (ketone, epoxide and

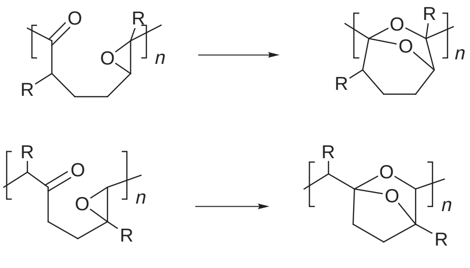

Fig. 4 The formation of bicyclic ketals with different ring sizes from epoxidised polybutadiene or polyisoprene

ketal) suggests that each kind of residue can be in two different chemical environments, although the complexity of the polymer does not allow us to distinguish what these might be.

Conclusion

We conclude that *cis*-polybutadiene or polyisoprene can be smoothly converted into polyepoxides in which all of the double bonds have been epoxidised, the best results being obtained with a catalyst prepared from $[MoO_2]^{2+}$ adsorbed on molecular sieves and with *tert*-butyl hydroperoxide as oxidant. These polymers can be isomerised to polyketones using LiBr in THF, but the products are either insoluble, probably as a result of extensive crosslinking *via* aldol type reactions (polybutadiene epoxides), or contain units obtained from intramolecular cyclic ketal formation between ketone and epoxide units (polyisoprene epoxides) in addition to ketonic functionality and unreacted epoxides.

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