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The metathetic degradation of polyisoprene and polybutadiene in block copolymers using Grubbs second generation catalyst

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ABSTRACT

A degradation study of polystyrene–polybutadiene–polystyrene and polyisoprene–polystyrene–polyisoprene in both dichloromethane and hexane solvents is presented. Alternative solvents for metathetic degradation provide the potential for greener chemistry, better selectivity, and control over the products. The catalyst concentration and solvent selection both determine the products formed. The degradation of polyisoprene and polybutadiene in a particular solvent was controlled by the solubility of polyisoprene/polybutadiene, and by its solubility relative to polystyrene. A large difference in solubility between the polymers in the selected solvent provides an additional driving force for block separation, encouraging reaction close to the interface between different blocks. Furthermore, solubility of the block copolymer speeds the degradation reaction. This tailoring of the reaction mechanism yields a new control over the products of polymer degradation.

1. Introduction

Over the past half century the development of transition metal centred catalysts for polymerization reactions has been an important area of organic chemistry. One of these processes is the acyclic diene metathesis (ADMET) polymerization. The research into this reversible reaction has focused on the use of monomer substrates for the formation of polymers. This is achieved by well understood mechanisms, with the transition metal centred catalyst forming a ring structure with carbon–carbon double bonds [1].

This catalysis was long believed to have stringent solvent requirements, and particularly water intolerance. With developments from early catalysts to those commonly available today (e.g. 2nd Generation Grubbs) significant differences have been shown to exist [1–3]. ADMET polymerizations have now become viable in a range of alternative solvents [4,5] to the originally used chlorinated solvents, including water [6,7]. Solventless polymerizations for monomers in the liquid phase have also shown promise. These developments are significant given the pressure of creating 'greener' processes [1–3].

Advances have primarily centred on the polymerization capabilities of the ADMET scheme [8–10]. More recently, interest has also focused on the reversible nature of this mechanism. In general, polymers are introduced and the catalyst is used to create lower molecular weight products. In fact, a complication lies in two methods for achieving this: metathesis degradation and ADMET depolymerization [11]. This work focuses on the former though the close link of the two is noted. Most studies have been limited to a single polymer (e.g. polybutadiene), where the success of metathetic degradation and ADMET depolymerization has been demonstrated [12–19]. Furthermore, performance has been compared for different catalysts and the influence of other factors. Unlike ADMET polymerization, the potential of metathetic degradation has yet to be fully explored. The degradation of copolymers containing saturated and unsaturated units has been reported [20–24]. Even more minimally studied is block copolymers, though [21] uses ADMET depolymerization.

This study is an initial exploration into the effect of solvent upon metathesis degradation of block copolymers. Given the nature of the starting material – a solid insoluble in a range of solvents – the results are not directly transferable to the reverse reaction. Degradation in dichloromethane and hexane are reported here.

2. Experimental methods

Two solid cylinder forming tri-block copolymers were investigated in this work. The first has a glassy continuous phase polymer:

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polystyrene–(1,4)polybutadiene–polystyrene (PB = 26%; referred to as PolyG) with a Mn of 90,000 g/mol and a PDI = 1.08. In contrast the second has a rubbery continuous phase: (1,4)polyisoprene–polystyrene–(1,4)polyisoprene (PS = 18%; PolyR) with an Mn of 160,000 g/mol and a PDI = 1.10. Polymers, solvents, and catalyst were all used as received.

2.1. Degradation

Polymer degradation was investigated in a 250 ml batch reactor (round bottom flask) with continuous N_2 flow. Reactions were carried out in either dichloromethane (DCM, Aldrich) or hexane (Aldrich) with 1.0 g block copolymer introduced at a concentration of 0.03 M of butadiene in PolyG and 0.08 M of isoprene in PolyR. The molarity is nominally larger in PolyR due to the weight fraction of isoprene in comparison to butadiene. The reaction was conducted at room temperature while stirring with a magnetic stir bar. Methanol and O_2 were used to quench the experiment.

The solvents (top row) and polymers (first column) investigated have the Hildebrand solubility parameters (cal$^{1/2}$/cm$^{3/2}$) shown in Table 1. The squared difference of solubility parameters is often used as an indication of the miscibility of two materials, a value of less than one usually taken as indicating complete miscibility [25].

2nd Generation Grubbs catalyst was introduced after the polymer in stoichiometric proportion to the quantity of carbon–carbon double bonds present in the polymer, as shown in Table 2. Solid catalyst was added directly into solvent. Catalyst was stored under N_2 to avoid its degradation. Significant variation occurs particularly when small quantities of catalyst are measured, particularly cases of lower catalyst ratio. Regardless, it was determined that repetitions of experiments showed good consistency and furthermore need not be reported separately.

Aliquots of the reacting mixture were sampled by syringe at time intervals. Large insoluble pieces were not sampled using the syringe, this was particularly true for samples in hexane which did not appear to dissolve. These insoluble components were sampled at the conclusion of the experimental trial (various times to obtain a series of results). Soluble polymeric materials sampled by syringe were precipitated. For experiments carried out in DCM this was accomplished by the addition of methanol (a good non-solvent for all polymers used – see Table 1) and filtration. This may have resulted in some losses of relatively low molecular weight polymer. This method proved less successful for collecting the soluble fraction from polymers dissolved in hexane due to the apparent miscibility with methanol. Thus the hexane was removed simply by decanting.

2.2. Characterization

Characterization was accomplished using Size Exclusion Chromatography (SEC) (GPCMax VE2001 GPC Solvent/Sample Module) and Nuclear Magnetic Resonance spectroscopy (NMR) (Bruker 400 MHz) in $CDCl_3$. For the former molecular weights were determined using triple detection SEC on a Viscotek 302 with refractive index, viscosity and light scattering detectors, and 2 × 300 mm PLgel 5 μm mixed *d* 0.144 were used for polystyrene and polyisoprene respectively. THF was used as the eluent with a flow rate of 1.0 ml per min and at a constant temperature of 35 °C. The detectors were calibrated with a single polystyrene standard (Polymer Labs) and values of dn/dc (ml g^{-1}) of 0.185 and 0.144 were used for polystyrene and polyisoprene respectively. Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet Nexus) was used for supporting information.

Table 1
Hildebrand solubility parameters (cal$^{1/2}$/cm$^{3/2}$) of solvents (δ_s) used (top row) and polymers (δ_p) (first column). The squared difference, $(\delta_s - \delta_p)^2$, is shown in the body of the table: a value of less than one is generally taken to indicate solubility and experimentally within a margin of error.

	DCM (9.7)	Hexane (7.3)	Methanol (14.5)
PS (9.1)	0.36	3.2	29
PI (8.1)	2.6	0.64	41
PB (8.4)	1.7	1.2	37
PolyG (PS–PB–PS)[a]	Soluble	Insoluble	Insoluble
PolyR (PI–PS–PI)[a]	Semi-soluble	Semi-soluble	Insoluble

[a] Solubility information for the polymers used was obtained experimentally.

Table 2
Experiments conducted on polymers at various catalyst concentrations with number of repetitions (n) and standard deviation. Symbols used in subsequent figures are also indicated.

Polymer	Solvent	Average ∼ C=C:catalyst		
		◇	□	△
PolyG	DCM	330:1 ($n = 2$)	3000:1 ($n = 5$)	39,000:1 ($n = 2$)
PolyR	DCM	[a]	1300:1 ($n = 2$)	11,000:1 ($n = 3$)
PolyG	Hexane	420:1 ($n = 2$)	1500:1 ($n = 3$)	[b]
PolyR	Hexane	[a]	1700:1 ($n = 2$)	13,000:1 ($n = 2$)

[a] Physical experimental constraints precluded these trials due to overabundance of catalyst. Decreased catalyst concentration by one order of magnitude already demonstrated an excess of catalyst.

[b] Trial failed due to inadequate catalyst.

3. Results

3.1. Degradation in dichloromethane

3.1.1. Molecular weight results

The degradation of both PolyG (PS–PB–PS) and PolyR (PI–PS–PI) in DCM has been investigated. The results of PolyG degradation are reported first, and are followed by that of PolyR. The effect of substrate (unsaturated polymer):catalyst ratio was investigated in both cases. For PolyG mole ratios of catalyst : C=C double bonds of ∼330:1, ∼3000:1, and ∼39,000:1 were used. The change in molecular weight of the polymer over time is displayed in Fig. 1a for all polymer/catalyst ratios. The data points represent the number average molecular weight (Mn). The error bars indicate the standard deviation of the molecular weight peak accounting for both multiple samples and the dispersity within each individual samples. The weight average molecular weight (Mw) is within this standard deviation.

The three horizontal lines in Fig. 1a indicate the approximate base molecular weight for specified components of the block copolymer. The lowest horizontal line at approximately 33,000 g/mol is for a single PS block. The middle line at 56,000 g/mol is for the di-block of PB–PS; that is after one PS block has been removed from the tri-block copolymer. The top line indicates the molecular weight (approx 90,000 g/mol) of the complete tri-block copolymer. The three data points labelled with Roman numerals in Fig. 1a are shown as size exclusion chromatograms in Fig. 1b. Note that the peaks remain fairly sharp as decomposition occurs, although some broadening is evident at point II, and a higher molecular weight tail remains at point III (Fig. 1b). This indicates that there are preferential scissions approaching the PS–PB interface before separation to PS blocks alone.

The extent and rate of tri-block copolymer degradation in DCM is dependent on catalyst concentration. At the highest ratio of PolyG to catalyst (∼39,000:1) the original tri-block copolymer undergoes decomposition to a product with the molecular weight of a PS–PB di-block copolymer (or approximately half of the total molecular weight of the original tri-block) over the timescale investigated. Note that a single double bond scission in PolyG will split the two PS blocks. When using a greater amount of catalyst by

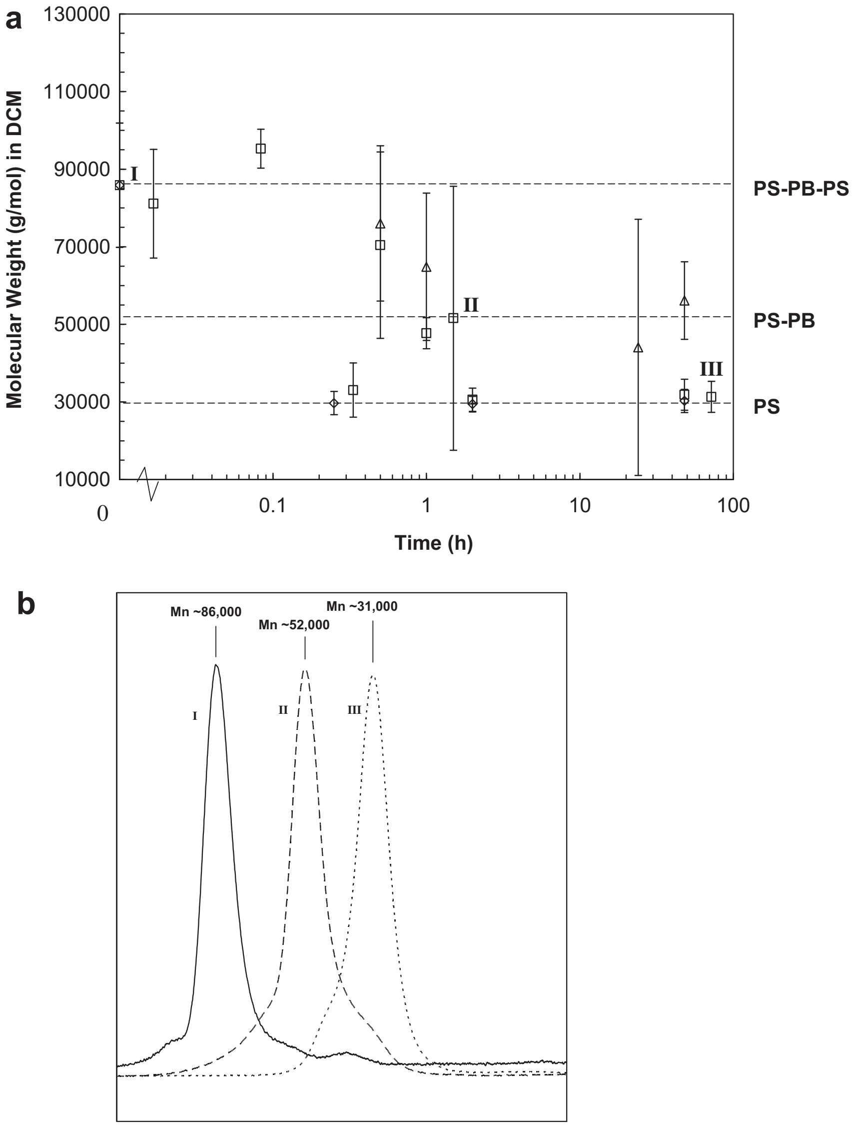

Fig. 1. (a) The change in molecular weight of PolyG under varying catalytic ratios in DCM where ◇ ~330:1, □ ~3000:1, and △ ~39,000:1. Error was measured as variance of samples at the same time point at the same catalytic ratio. Error bars represent one sigma. Only peaks >10,000 g/mol are shown. (b) The SEC chromatogram for three peaks shown in (a). **I**: PolyG before reaction, **II**: one and a half hours after the start of the reaction at polymer to catalyst ratio ~3000:1, **III**: 72 h after the start of the reaction at polymer to catalyst ratio ~3000:1.

decreasing the PolyG/catalyst ratio to ~3000:1, a product with the same molecular weight as above is obtained after approximately 0.5–1 h. At longer times further degradation occurs, eventually resulting in a product similar in molecular weight to a single PS block. At the highest ratio of catalyst to PolyG (~1:330) a molecular weight corresponding to a single PS block is observed after a very short period of time, <0.5 h.

A similar analysis to that described above for PolyG was also carried out for PolyR. In this case the substrate to catalyst ratios were ~1300:1 and ~11,000: 1. PolyR has the inverse structure to that of PolyG, with two unsaturated blocks (of polyisoprene) surrounding an inert central block of PS. Fig. 2a shows the results of the decrease in molecular weight function of time. The lowest of the horizontal lines at 30,000 g/mol corresponds to an individual PS block. The middle of the three lines at 95,000 g/mol is the molecular weight of a PI–PS di-block (after one PI block is removed). The top line, at 160,000 g/mol is the molecular weight of the complete tri-block copolymer PI–PS–PI. As was previously shown, the data points represent the molecular weight number average (Mn) and the error bars indicate the standard deviation of the molecular weight peak accounting for both multiple samples and the dispersity within each individual samples.

Fig. 2b shows four size exclusion chromatograms for points labelled with Roman numerals in Fig. 2a. Initially the peak shifts to lower molecular weight, corresponding approximately to a PS–PI di-block, with little broadening. Further degradation is accompanied by substantial peak broadening.

A qualitatively similar dependence of degradation of polymer on catalyst ratio is observed for Poly R when compared to that observed for PolyG. At the lower ratio of catalyst (~1:11,000) the tri-block copolymer forms a species with the molecular weight of approximately a di-block and no further degradation is observed until beyond 10 h, after which the molecular weight decreases towards that of the PS block. Furthermore, the process is definitively refined as the time increases this order of magnitude as seen by the significant decrease in error. The higher catalyst ratio (~1:1300) results in the formation of species with the molecular weight a single PS block.

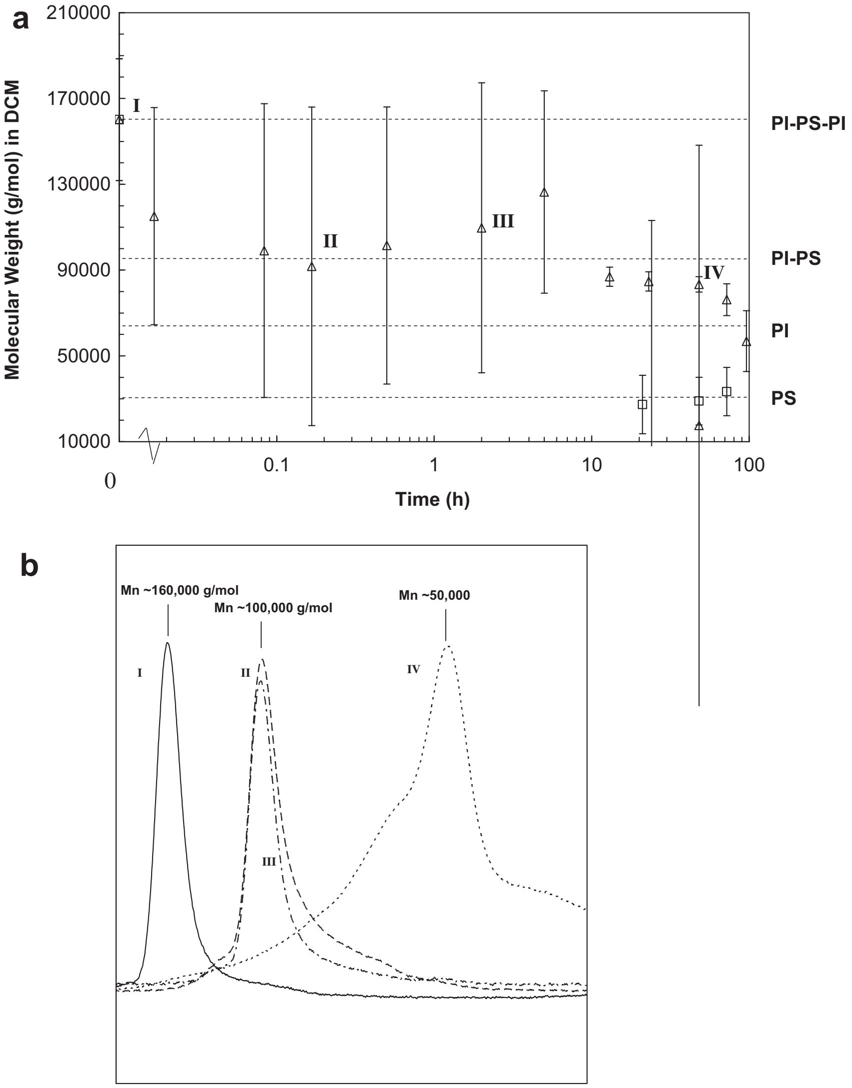

Fig. 2. (a) The change in molecular weight of PolyR under varying catalytic ratios in DCM where □ ~1300:1 and △ ~11,000:1. Error was measured as a variance of samples at the same time point at the same catalytic ratio. Only peaks >10,000 g/mol are shown. (b) The SEC chromatogram for four peaks shown in (a). **I**: PolyR before reaction, **II**: 10 min, **III**: 2 h, and **IV**: 48 h after the start of the reaction at a ratio of ~11,000:1.

3.2. Degradation in hexane

3.2.1. Molecular weight analysis

In order to probe the influence of solvent on the reaction, the degradation of PolyG and PolyR has also been studied in hexane. In contrast to DCM, hexane (Table 1) is not expected to dissolve the catalyst – this is confirmed by visual inspection of the catalyst in the solvents. The catalyst is purple and naturally dyes a solvent when dissolved. This is not observed in hexane; rather, the small particles of catalyst remain undissolved and the hexane remains clear. Fig. 3a shows molecular weight changes for PolyG in hexane with two ratios of catalyst: ~1:420 and ~1:1500. The multiple data points at specific times are due to bimodal and trimodal molecular weight distributions. The horizontal lines are the same as those indicated in Fig. 1a and described above.

The data from both catalyst ratios across all times are clustered around the three horizontal lines indicating the molecular weights of the polymer blocks. In the case of lower catalyst to polymer ratio (~1:1500), the molecular weights of unreacted PS–PB–PS tri-block, PS–PB di-block and PS alone are observed. For the higher catalyst ratio (~1:420), the tri-block and single PS block predominate. The alternative presentation of the data in Fig. 3b clearly demonstrates that the size exclusion chromatography peaks are genuinely bi- or trimodal, indicating preferential scission of double bonds close to the PS–PB boundary. The time evolution to lower molecular weight is also more clearly evident in Fig. 3b than a.

PolyR in hexane was also studied at substrate to catalyst ratios of ~1700:1 and ~13,000:1. The change in composition is shown in Fig. 4a and b.

The molecular weight distribution of the samples (measured by SEC) at 3 h (**II**) and 48 h (**III**) for a catalyst ratio of ~13,000:1 is shown in Fig. 4b. A broad distribution of molecular weights is rapidly formed and maintained over the course of the reaction. The lower molecular weight peak, visible after 48 h, corresponds to small fragments of PI.

3.2.2. NMR results

Fig. 5a and b shows the NMR spectra of the polymers before reaction and the separated solid and solution components after the completion of the reactions, for PolyG and PolyR respectively.

Before reaction, in both cases, peaks are visible for both alkene (4.5–6.0 ppm) and aromatic groups (6.0–7.5 ppm). The soluble fraction shows an increase in the relative intensity of alkene groups

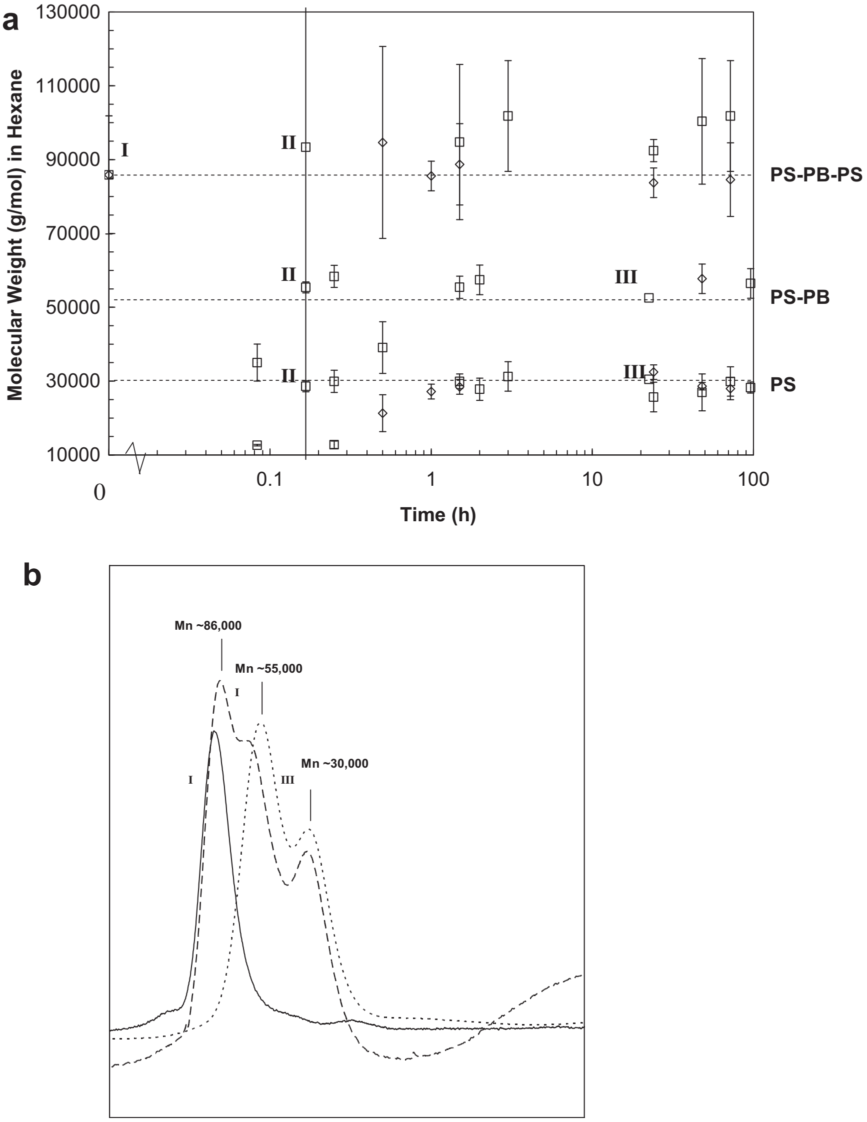

Fig. 3. (a) The change in molecular weight of PolyG under varying catalytic ratios in hexane where ◇ ∼420:1 and □ ∼1500:1. Unimodal, bimodal, and trimodal peaks are plotted as measured. Error was measured as variance of samples at the same time and concentration. A finely tuned bracketing (binning) method was used to maintain the integrity of the data. Plotted data includes all peaks >10,000 g/mol contained in each repetition.(b) The SEC chromatogram for three peaks shown in (a). **I**: PolyG before reaction, **II**: 10 min, **III**: 22 h 30 min after the reaction at polymer to catalyst ratio ∼1500:1.

relative to aromatic ones, whilst the solid fraction shows increased intensity in the aromatic region. This is relatively consistent with the solubility of PB and PI, but insolubility of PS, in hexane (as expected from Table 1) and the separation of the PS blocks from the unsaturated ones as the reaction proceeds. Note that the solid–liquid separation is achieved by decantation and so is not perfect, accounting for the presence of aromatic peaks in the solution fraction.

4. Discussion

We report metathesis degradation of two block copolymers in two solvents. In DCM the metathesis catalyst is soluble, as are the PS blocks of the polymers; however the PB or PI blocks are relatively insoluble (by comparison, Table 1) – overall PolyG (PS–PB–PS) is expected to be soluble in DCM. In contrast PolyR (PI–PS–PI) will be relatively insoluble. In hexane the situation is reversed: the catalyst is insoluble, PB and PI are soluble, PS insoluble. Overall PolyG is expected to have low solubility in hexane. One might expect the polymer to swell due to the ingress of solvent into the polybutadiene domains, whereas PolyR should have comparatively high solubility. The separation is a function of solvent–polymer and polymer–polymer interactions which encourages (or discourages) cleavage of the reactive component. This is most clearly seen in the case of PolyG, PolyR giving much broader molecular weight distributions, indicating that double bonds are reacting at many points along the unsaturated chain. Previous studies [22–24] have suggested that a backbiting mechanism resulting in cyclic alkenes may be in play.

In the case of PolyG in DCM, we expect the reaction to occur in the bulk of the liquid, since both the catalyst and polymer are soluble. There is evidence in the literature [26,27] that block copolymers form micelles when the two blocks have significantly different solubilities in the solvent. In this case we expect a core of insoluble PB surrounded by a solvated shell of PS. Access by the catalyst to the reactive PB will therefore be possible only at the

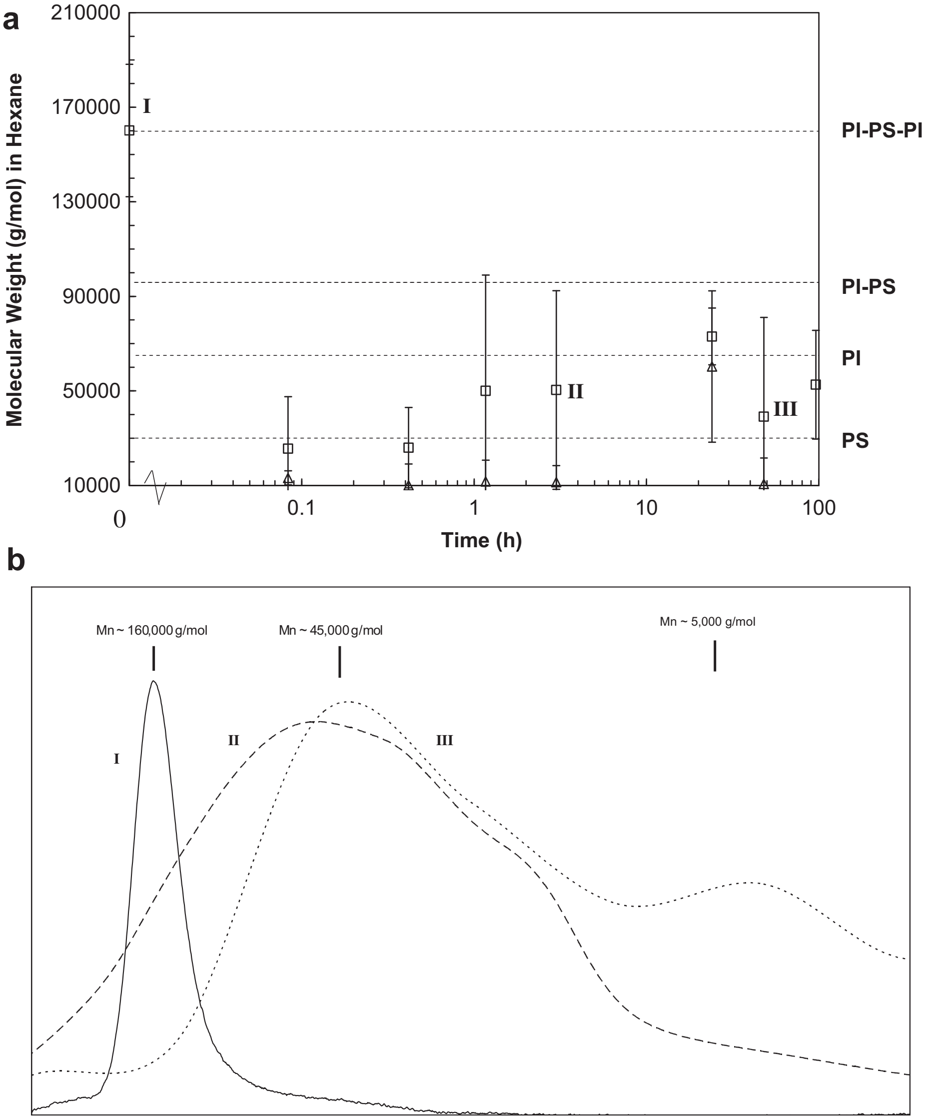

Fig. 4. (a) The change in molecular weight of PolyR under varying catalytic ratios in hexane where □ ~1700:1 and △ ~13,000:1. (b) The SEC chromatograph for the three peaks shown where **I**: PolyR before reaction, **II**: 3 h, **III**: 48 h after the start of the reaction at a catalytic ratio of ~13,000:1.

PB–PS interface, explaining the lag in time for reaction to occur. In fact, this mass transfer limitation shows no vastly increased rate of reaction by concentration of catalyst.

For PolyG in hexane, the reaction can only occur at the solid–liquid interface, since the catalyst is now insoluble. Thus the reactive molecules are those at the liquid interface. We expect these to consist of PS (poorly soluble in hexane) chains outside the liquid, with solvated PB in the surface layer of the liquid. Even due to its insolubility, the catalyst will be available for cleavage of the reactive species.

In the case of PolyG, the steric factors just described are strong because the molecule contains more PS then PB (each of the two PS blocks has around 300 monomer units, the central PB block has about 370 butadiene sub-units) – thus the behaviour can be dominated by the inert PS limiting the access of the catalyst to the reactive double bonds. There may also be a thermodynamic driving force encouraging reaction, particularly near the block interface, when there is a large solubility difference between the two blocks: splitting the blocks will result in a reduction in free energy of solvation.

The behaviour of PolyR is analogous (but reversed; since this molecule is more soluble in hexane than DCM), but the steric effects are weaker because the PolyR molecule consists mainly of unsaturated chains – the single PS block is again about 300 sub-units long, whilst each of the two PI block contains approximately 950 sub-units. Thus the steric effects caused by the unreactive block are relatively smaller than in the case of PolyG, and the catalyst is able to attack more freely along the PI chains. The PI is protected by a nominal solvating shell of PS. Following this, the detection of lower molecular weight products here by comparison to PolyG in DCM is unsurprising.

The reaction proceeds vastly differently when the polymer is soluble (PolyG in DCM and PolyR in hexane) than when it is relatively insoluble. This is the alternate case to the previously described as controlled by mass transfer limitations of catalyst reaching the surface of C=C containing polymer. The higher mobility of the polymer in solution allows the catalyst easier access. As a medium of transport, the solvent, and its direct impact on catalyst rate of reaction is difficult to deduce from the information gathered here.

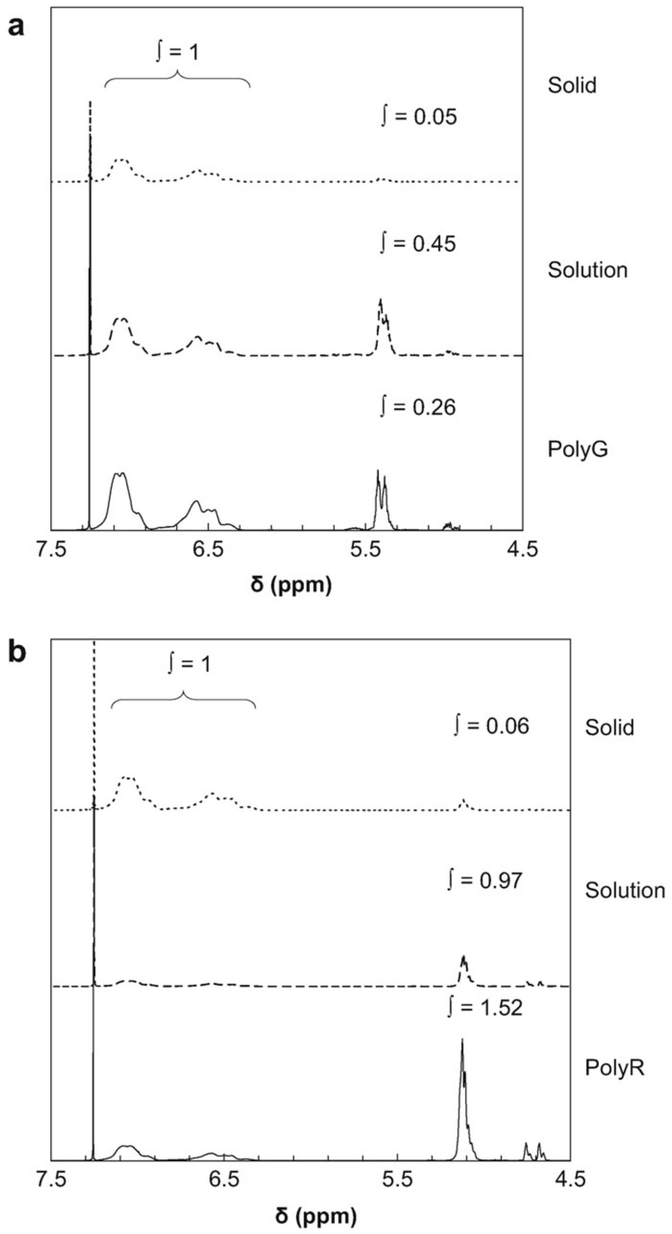

Fig. 5. (a) The composition of solid and solution products compared to PolyG by NMR. At 22 h 30 min (Fig. 4a and b **III**). (b) The composition of the solid and solution products compared to PolyR by NMR at 48 h (Fig. 4a and b **II**I).

4.1. Conclusions

The success of metathesis degradation for two different block copolymers in two different solvents has been demonstrated. Significantly different reaction rates were observed for the degradation under conditions in which the polymer was soluble and insoluble. Differential solubility of the two types of block in the polymers provides a driving force, both thermodynamic and probably more importantly steric, to scission close to the interface between blocks. The interplay between the catalyst mechanism and solubility of polymer in determining the reaction products introduces the potential for a new control mechanism in metathesis degradation.

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References

[1] Furstner A, Ackerman L, Gabor B, Goddard R, Lehmann CW, Mynott R, et al. Chem Eur J 2001;7:3236–53.
[2] Courchay FC, Sworen JC, Wagener KB. Macromolecules 2003;36(22):8231–9.
[3] Kniese M, Meier MA. Green Chem 2010;12(1):169–73.
[4] Stark A, Ajam M, Green M, Raubenheimer HG, Ranwell A, Ondruschka B. Adv Synth Catal 2006;348(14):1934–41.
[5] Nguyen S, Johnson L, Grubbs RH. J Am Chem Soc 1992;114(10):3974–5.
[6] Zaman S, Curnow O, Abell A. Aust J Chem 2009;62(2):91–100.
[7] Binder J, Blank J, Raines R. Org Lett 2007;9(1):4885–8.
[8] Smith Jr DW, Wagener KB. Macromolecules 1993;26(7):1633–42.
[9] Hofmann P, Volland MAO, Hansen SM, Elsentrager F, Gross JH, Stengel KJ. Organomet Chem 2000;606(1):88–92.
[10] Mecking S, Held A, Bauers F. Angew Chem Int Ed 2002;41(4):544–61.
[11] Wagener KB, Puts RD, Smith Jr DW. Makromol Chem Rapid Commun 1991;12:419–25.
[12] Marmo J, Wagener K. Macromolecules 1995;28(8):2602–6.
[13] Marmo J, Wagener K. Macromolecules 1993;26(8):2137–8.
[14] Reyx D, Campistron I. Angew Macromol Chem 1997;247:197–211.
[15] Fraser C, Hillmyer MA, Gutierrez E, Grubbs RH. Macromolecules 1995;28(21):7256–61.
[16] Watson M, Wagener KJ. J Polym Sci A Polym Chem 1999;37(12):1857–61.
[17] Marciniec B, Lewandowski M, Gulinski J, Noels AF, Demonceau A, Matecka E, et al. Polymer 2000;41(3):827–30.
[18] Marciniec B, Malecka E, Gulinski J, Grundwald-Wyspianska M, Lewandowski M. Can J Chem 2001;79(5–6):775–9.
[19] Solanky S, Campistron I, Laguerre A, Pilard J. Macromol Chem Phys 2005;206(10):1057–63.
[20] Thanki P, Reyx D, Campistron I, Laguerre A, Singh RP. Eur Polym J 2004;40(11):2611–6.
[21] Craig SW, Manzer JA, Coughlin EB. Macromolecules 2001;34(23):7929–31.
[22] Lucas F, Peruch F, Carlotti S, Deffieux A, Leblanc A, Boisson C. Polymer 2008;49(23):4935–41.
[23] Thorn-Csanyi E, Abendroth H, Perner H. Makromol Chem 1980;181(10):2081–9.
[24] Thorn-Csanyi E, Perner HJ. Molec Cat 1986;36(1–2):187–99.
[25] New York. In: Brandrup J, Immergut EH, editors. Polymer handbook. Interscience Publishers; 1966.
[26] Awan MA, Dimonie VL, Ou-Yang D, Aasser MS. Langmuir 1997;13(2):140.
[27] Nunes SP, Sougrat R, Hooghan B, Anjum DH, Behzad AR, Zhao L, et al. Macromolecules 2010;43(19):8079–85.