

# The photoinitiated cyclopolymerization of dienes in the creation of novel polymeric systems and three-dimensional networks†

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Received 11th February 2004, Accepted 7th May 2004

First published as an Advance Article on the web 23rd July 2004

In this article we describe the photo-initiated cyclopolymerization of 5-, 6- and 7-centre dienes. We find that substituted dienes can be cyclopolymerized in sunlight or by the use of a low-power UVA sunlamp of broad spectral range (320–400 nm). Unless activated by suitable electron withdrawing groups the cyclopolymerization can often be slow and incomplete. However, when suitably activated the polymerization rates can approach those for acrylates. In particular diallylamine, its quaternary salts, which can often be obtained as ionic fluids, and diallylamide, can be subjected to fairly rapid photocyclopolymerization to give robust coatings and adhesives. This discovery augments, and gives a different

dimension, to the acrylate and methacrylate monomer and polymer systems that are already commercially available.

## 1. Introduction

The development of environmentally friendly materials and processing technologies are seen by many as being pivotal to the future of the chemical industry in Europe. In particular, processes which are free of organic solvents or are water-based are seen to be increasingly desirable. UV-curable polymer systems are thus of considerable interest in the development of coatings, adhesives, thin-films and smart materials. The range of UV-curable systems is however limited, with acrylates and

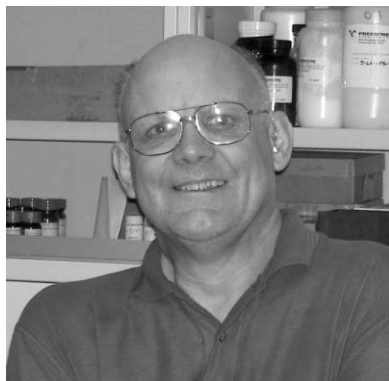
† Electronic supplementary information (ESI) available: Experimental details. See <http://www.rsc.org/suppdata/jm/b4/b402154c/>

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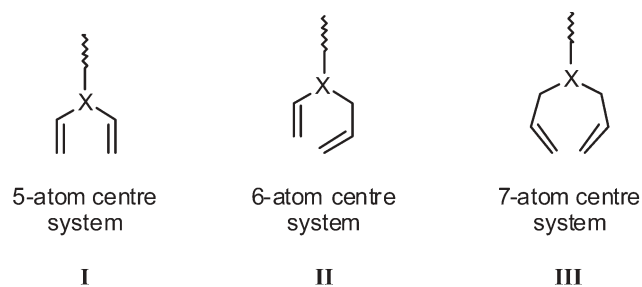
Alan W. Hall



Mark J. Godber



Keith Blackwood



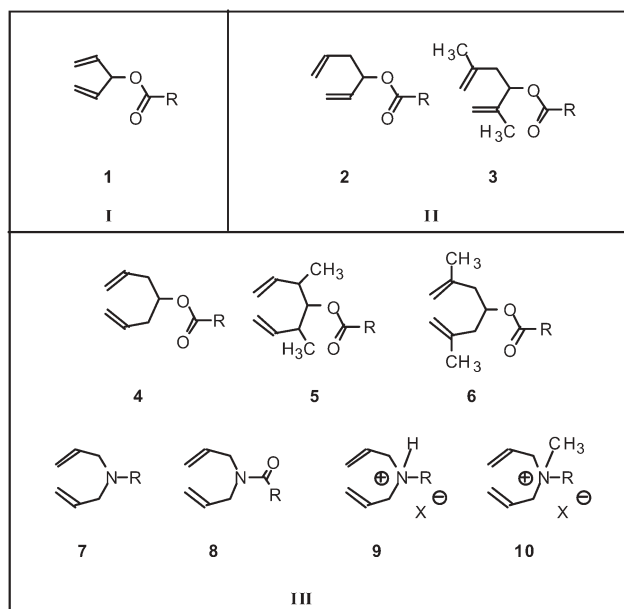
**Fig. 1** General structures of dienes which were subjected to cyclopolymerization.

methacrylates being the most popular choice for use by industry because of their low cost, ease of derivatization and speed of processing. However, the use of such prepolymers can tend, in some cases, to limit the properties of the final polymer product. In this article we describe the development of new classes of UV-curing polymeric systems, based on dienes, that have significantly different properties to those of acrylates and methacrylates, such as adhesion to metal surfaces, but which have the same virtues of low cost, ease of derivatization and processing. For example, dienes, such as diallylamine, are easily functionalized and can undergo cyclopolymerization to give polymers with more rigid backbones than acrylates or methacrylates.<sup>1</sup> In addition, the quaternary salts of substituted diallylamines can be designed to exist as ionic liquids, thereby imparting them with uniquely different structures and properties to acrylates and methacrylates.

The significance of intramolecular cyclization of unconjugated dienes was highlighted in the 1950's when Butler *et al.*<sup>2–5</sup> discovered that free radical *solution* polymerization of diallyl quaternary ammonium salts gave soluble, uncrosslinked polymers with only a very small amount of residual unsaturation. Butler *et al.* demonstrated that intramolecular cyclization occurs during the polymerization of unconjugated dienes, in general, to form linear polymer chains consisting of cyclic structures composed of either five- and/or six-membered heterocyclic rings. The resulting polymers were subsequently found to be of considerable industrial importance in ion exchange resins for chromatography and water purification systems *etc.* Similarly, we have demonstrated, using <sup>1</sup>H NMR, that the free radical initiated photopolymerization of unconjugated dienes is also a cyclopolymerization process.

In this feature article we will describe the cyclopolymerization of three different types of diene systems that have structures based upon the number of atoms between, and including, the terminal carbon atoms of the diene units. Thus we examined the cyclization of dienes possessing five (I), six (II) and seven (III) atom centres, as shown in Fig. 1.

Structures 1 to 10 show examples of generic substituted dienes which were prepared and subjected to photocyclopolymerization. System 1 is an example of structure I; 2 and 3 are examples of structure II; and the most extensively studied systems 4 to 10 are examples of structure III.



All such monomeric diene units have an inherent ability to form linear chains and three-dimensional networks in the same polymerization process, thereby engendering the resultant materials with different physical and engineering properties to their acrylate and methacrylate analogues. Indeed, three-dimensional networks can be prepared easily through the cyclopolymerization of monomers that contain at least two diene units, as shown in Fig. 2. Furthermore, copolymerization of monomers possessing different diene units and/or substituents is also feasible, and in the case of monomers of type 8 and 9, we have shown it is possible to

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EO Signature Assessment and Control team. Since 1993, Dr Milne has worked on a wide variety of topics from materials deposition, electrochromism, paint technology, surface optical modelling and measurement and polymer technology. Dr Milne is currently the Leader of the Device Technologies team within the Thermal Imaging and Signatures Business Group at QinetiQ (Malvern).

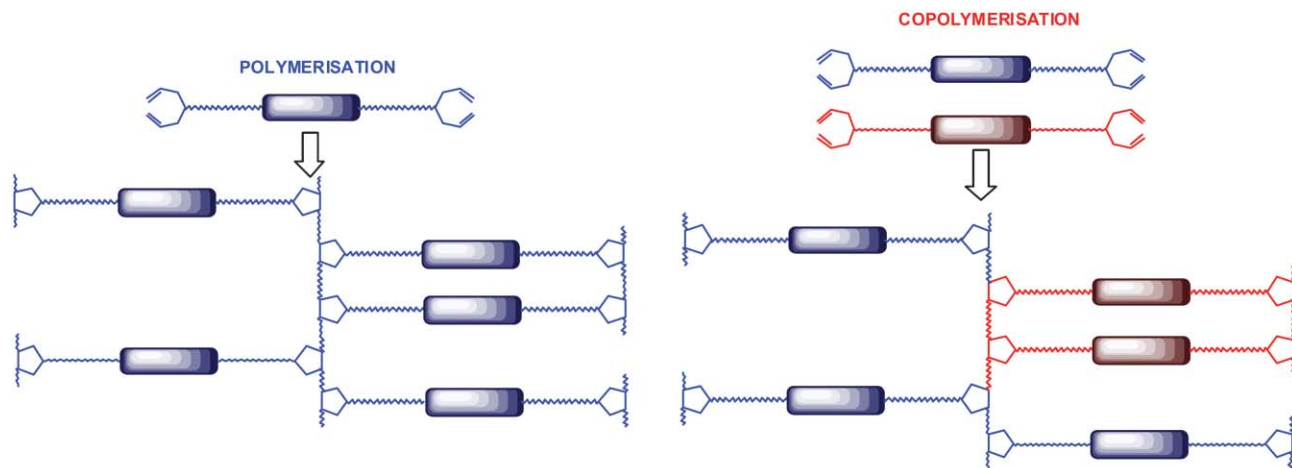
Professor John W. Goodby is currently the President of the

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of the Liquid Crystals Materials Group. In 1996 he was the first recipient of the GW Gray Medal of the British Liquid Crystal Society, in 1994 he was the Amersham Senior Research Fellow of the Royal Society, in 2002/3 he was the Tilden Lecturer of the Royal Society of Chemistry, and in 2002 he was awarded an Honorary Doctorate from Trinity College Dublin.



**Fig. 2** Three dimensional homo- and co-polymeric networks can be prepared easily through the cyclopolymerization of monomers that contain at least two diene units.

create mixed ionic/non-ionic copolymers without microphase segregation.

## 2. Mechanistic descriptions of the photo-initiated polymerization process

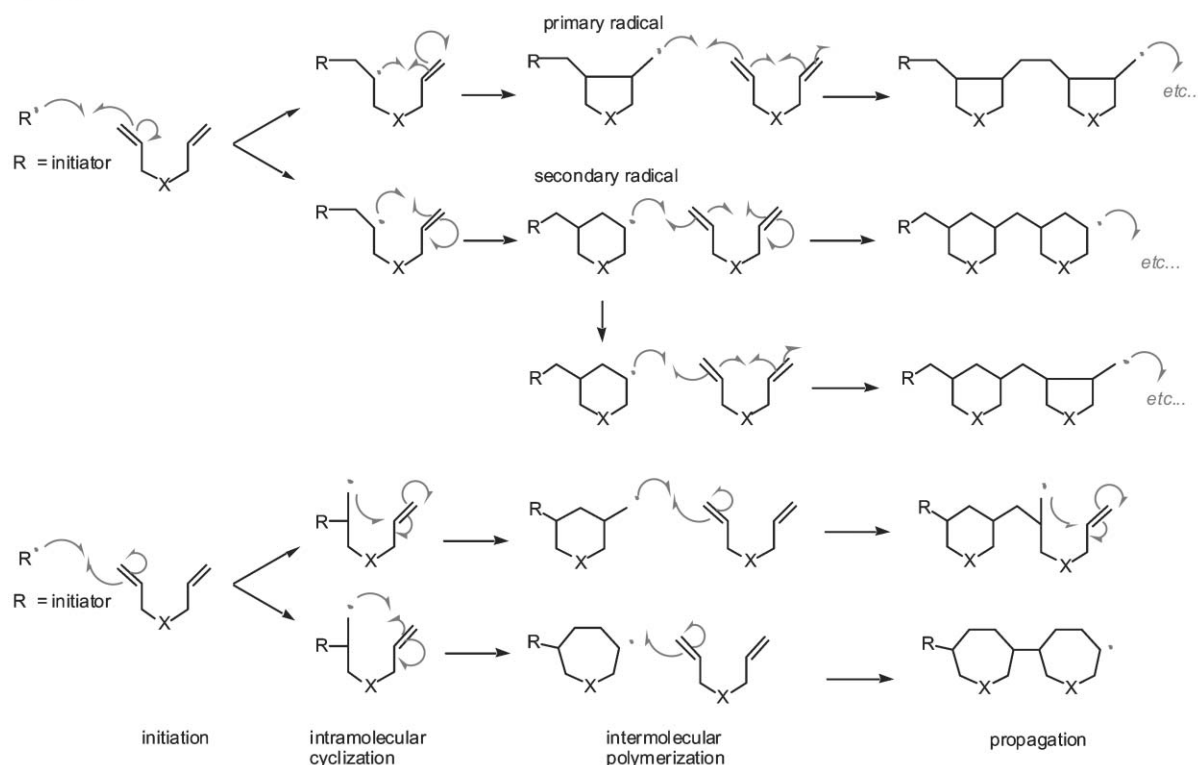
The polymerization procedure can be best described by an *alternating intra-inter-molecular polymerization* mechanism, but the processes for systems **I** to **III** have the potential to produce very different polymers depending on the initiation step and stability of the free radicals produced in the intra- and inter-molecular cyclization, as follows:

### 2.1 Cyclopolymerization of seven atom centre systems (III)

Initiated cyclopolymerization of seven atom centre systems is exemplified in Fig. 3 for an unspecified substituted diene.

Originally Butler *et al.*<sup>2-5</sup> described this process before the invention of mechanistic arrows, and, so for the first time, we give a full description of the cyclopolymerization using such mechanistic tools. This procedure can be used to describe the solution and neat thermal and radiation activated cyclopolymerizations of compounds **4** to **10** inclusive, where five-membered rings are most easily formed and predominate.<sup>6-8</sup> The predominance of five-membered rings can be rationalized in the following way; in the mechanisms shown in Fig. 3, the formation of the linear polymer consisting of five-membered rings requires the production of a primary radical intermediate, as shown. Conversely, the generation of the six-membered ring system necessitates the formation of the more thermodynamically stable secondary radical. The second process would be disfavoured in the situation where the polymerization process is kinetically controlled, which is probably the case due to the conformational structure of the intermediate obtained before

Cyclopolymerization of dienes with seven atom centres



**Fig. 3** The initiation process and propagation of the photocyclization reaction of substituted dienes with seven atom centres.

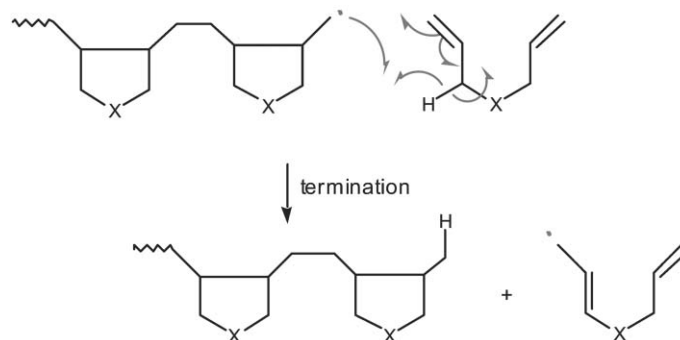


Fig. 4 The termination of the polymerization process by chain transfer degradation.

polymerization occurs. The regio-selectivity and stereo-selectivity in such radical reactions are not described by Baldwin's rules for ring closures, however, they have been explained in more detail by Beckwith.<sup>9</sup>

Much less likely is the formation of seven-membered ring structures as shown at the foot of Fig. 3. The creation of such ring structures depends first on the formation of a primary radical, and then subsequently, secondary radicals associated with the seven-membered ring systems. Ultimately, directly linked ring systems are created along the polymer backbones, which seems very unlikely due to the rigidity of the backbone of the polymer as it forms.

Consequently, polymer backbones incorporating both five- and six-membered ring systems, and to a lesser extent seven-membered rings are possible (as shown in Fig. 3), and indeed are likely to occur to give mixed systems which will increase the disordering of the system, and hence the associated entropy, of the polymer network. Furthermore, in both cases the degree of polymerization (DP) will be limited by *chain transfer degradation*, where the growing polymer chain is terminated by abstraction of an allylic hydrogen instead of reacting with a monomer vinyl group as shown in Fig. 4.

Physical evidence for the formation of various cyclic ring structures being formed along the polymer backbone was gained by Hall and co-workers from recent studies on the synthesis of side chain liquid crystal polymers derived from substituted dienes.<sup>10</sup> For example, Fig. 5 shows a schematic structure of a mesogen, **11**, created *via* the use of Baylis–Hillman technologies.<sup>11</sup> When subjected to cyclopolymerization such dienes produce a mixture of polymers containing 5- and 6-membered lactone rings, *i.e.* see structures **12** and **13** respectively. When the mesogenic unit was based on 4'-decyloxy-4-cyanobiphenyl, infra-red spectroscopy showed two carbonyl peaks at 1740 and 1685  $\text{cm}^{-1}$  corresponding to the respective formation of the 5- and 6-membered lactone rings, see Fig. 6. The lower part of Fig. 6 shows the infra-red

spectrum of the unreacted monomer for comparison, only one carbonyl adsorption band was found for this material.

The 5-membered ring adsorption occurs at a higher wave number due to ring strain, and the relative intensities of the absorptions of the carbonyl functions of the two lactones provide an indication of the relative proportions of the two present in the polymeric product. Although the five-membered lactone clearly predominates, there is still a substantial amount of the six-membered ring formed.

NMR spectroscopy was also used to show that both 5- and 6-ring systems are formed in the cyclopolymerization of dienes derived *via* Baylis–Hillman methodologies.<sup>11</sup>  $^1\text{H}$  NMR spectroscopy (270 MHz), as expected, gave little information concerning the 5-membered ring lactone due to the rigidity of the structure and the consequent efficiency of the nuclear relaxation in the  $^1\text{H}$  NMR experiment. Conversely, because of the flexibility associated with the six-membered lactone ring more information was available from the spectrum. For the hydrogen marked  $\text{H}_a$  in structures **14** and **15** two singlets of equal intensity were obtained at 3.60 and 3.75 ppm due to the formation of the racemic mixture in the Baylis–Hillman reaction.<sup>11</sup> The different shift values depend on whether the proton is *trans* (**14**) or *cis* (**15**) to the CN group, which produces a local magnetic anisotropic effect in the applied magnetic field. This influences the chemical shift value of the protons which are near enough to the cyano group to be influenced by this effect, *i.e.*  $\text{H}_a$  in **14** but not for **15**. This effect is, of course, not observed for the monomer since the CN group is not fixed in position by the ring structure. Furthermore, this result also confirms that cyclization has taken place in the polymerization reaction.

## 2.2 Cyclopolymerization of six atom centre systems (II)

Cyclopolymerization of six atom centre systems, such as compounds of type **2** and **3** (see structure **II**), follows the same

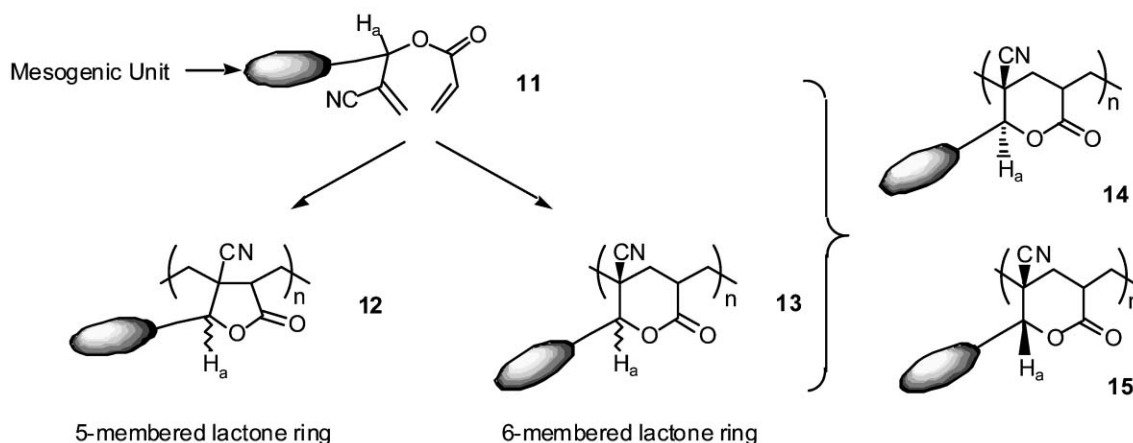
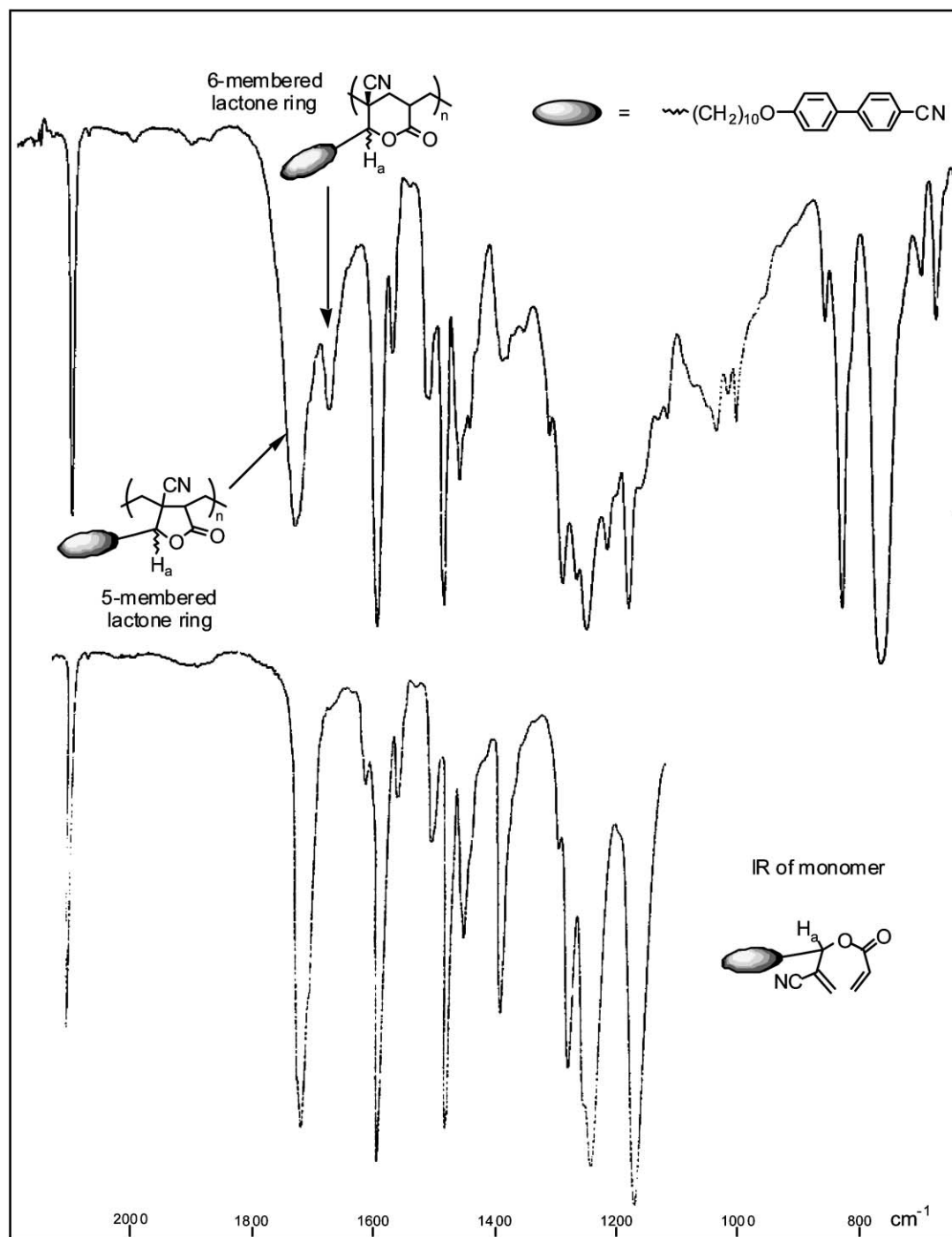


Fig. 5 Formation of five and six-membered lactone rings showing the relative stereochemical structures.





**Fig. 6** IR spectra of the monomer and polymerization product of **11**. The upper spectrum of the polymeric product shows the relative absorptions of the carbonyl groups in the five- and six-membered lactone rings formed by cyclopolymerization of dienes derived *via* the Baylis–Hillman reaction. The lower spectrum of the monomer shows only one carbonyl absorption band as expected.

mechanistic path as that for the formation of the five- and six-membered rings systems as shown in Fig. 7. Here though, the cyclopolymerization can give a wider variety of products due to the location of potential substituents (OX) attached to the monomer. Obviously the chemical nature of the substituent will affect the orientation of such groups in the final products, such that the substituents may be regularly or irregularly positioned along the backbone. Again five-membered and six-membered rings can feature in the same polymer backbone thereby increasing disordering effects and increasing the entropy of the system. For a polymer containing only five-membered rings there will be methylene units linking the rings together thereby providing flexibility of the material, whereas for six-membered ring systems, the rings will be directly linked giving a more rigid

polymer backbone. The rigidity of the six-membered systems thus makes them more unlikely to be formed. Seven-membered rings are, of course, not possible with six atom centre systems. Consequently, the products of six atom centre systems might be expected to have similar properties to those obtained with seven atom centre systems, except that the less flexible backbones will create more brittle materials.

Polymer networks have been, however, created through the cyclopolymerization of mesogenic monomers that possess two polymerizable groups as shown in structure **16**.<sup>12</sup> The rates of the cyclopolymerization processes for these materials were compared with the polymerization of the analogous bis-acrylates. It was found that the acrylate polymerization was over in 15 s, whereas the cyclopolymerization of the diene took

## Cyclopolymerization of dienes with six atom centres

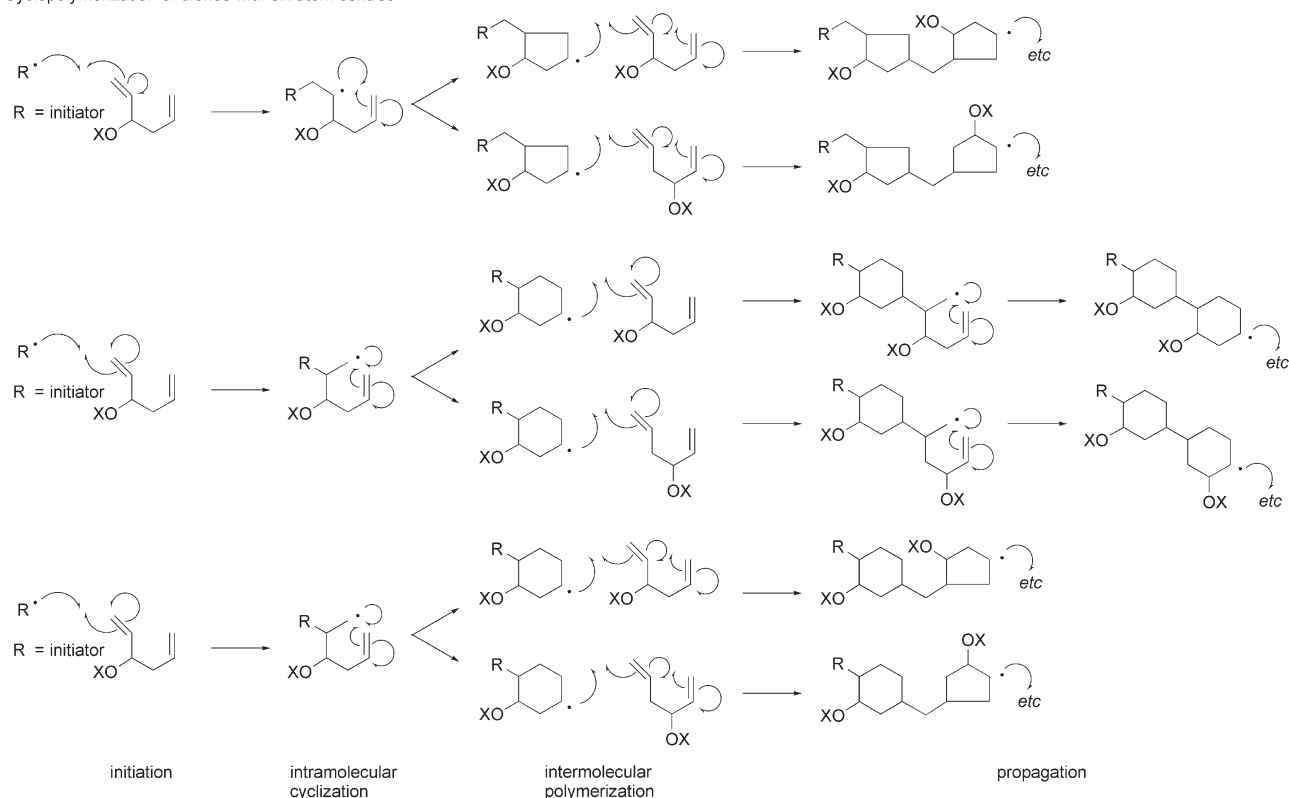


Fig. 7 The initiation process and propagation of the photocyclization reaction of substituted dienes with six atom centres.

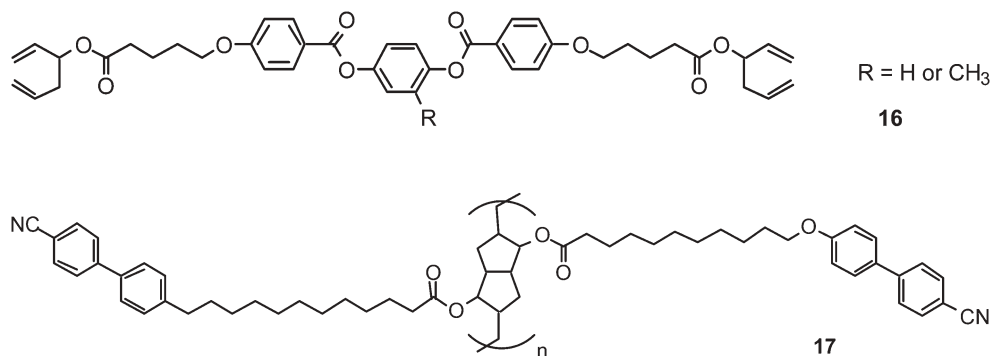
approximately 10 min. Furthermore, the polymerization processes were investigated by IR-spectroscopy, and after 1 min of irradiation the vinyl absorption of the bis-acrylate had totally vanished, whereas the absorption for the diene, although becoming visibly smaller does not completely disappear, indicating some unreacted groups remain in the polymer network. This result indicates that such dienes are not activated enough for complete reaction to occur as demonstrated by Hall *et al.* in previous studies<sup>10</sup> (see later).

### 2.3 Cyclopolymerization of five atom centre systems (I)

Cyclopolymerizations of five atom centre systems, *i.e.* for compounds of type **1**, are far more complex with many more products becoming possible. Fig. 8 gives various mechanistic rationales for the cyclization of substituted dienes of structure **I**. Unlike the cyclopolymerization of six- and seven-atom centre systems, the cyclization of **I** involves a two molecule process, which leads to the formation of polymeric bicycloalkyl systems. Similarly, Tsukino and Kunitake had shown that analogous results could be obtained *via* the radical cyclopolymerization of divinyl ethers, with bicycloalkyl systems being afforded.<sup>13</sup>

The combinations of primary and secondary radical formation, results in potentially five bicycloalkyl products (**A** to **E** in Fig. 8) being formed, and if we concern ourselves with the details of the stereochemistries of the products, this number rises to approximately twenty. If we apply Baldwin's rules to such mechanistic processes, then the most likely product is the simple bicyclopentyl product **A**, however, as we are dealing with a free-radical process rather than a polar mechanism, we can expect that many of the other products are also formed in small amounts. Indeed Hall *et al.* comment on the synthesis of side chain liquid crystal polymers of structure **17**,<sup>10</sup> that the products were isolated by solvent extraction, centrifugation, filtration and precipitation. Although the products had structures based on product **A** shown in the mechanism in Fig. 8, the fact that they were isolated from intractable material suggests that products from alternative cyclizations and cross-linking were also present.

Thus for materials such as **17**, it is possible to obtain relatively pure polymers, but in the creation of polymeric networks, as shown in Fig. 2, the products from alternative cyclizations will be fixed into the structure of the network, and not separable. In addition there will be unreacted double bonds



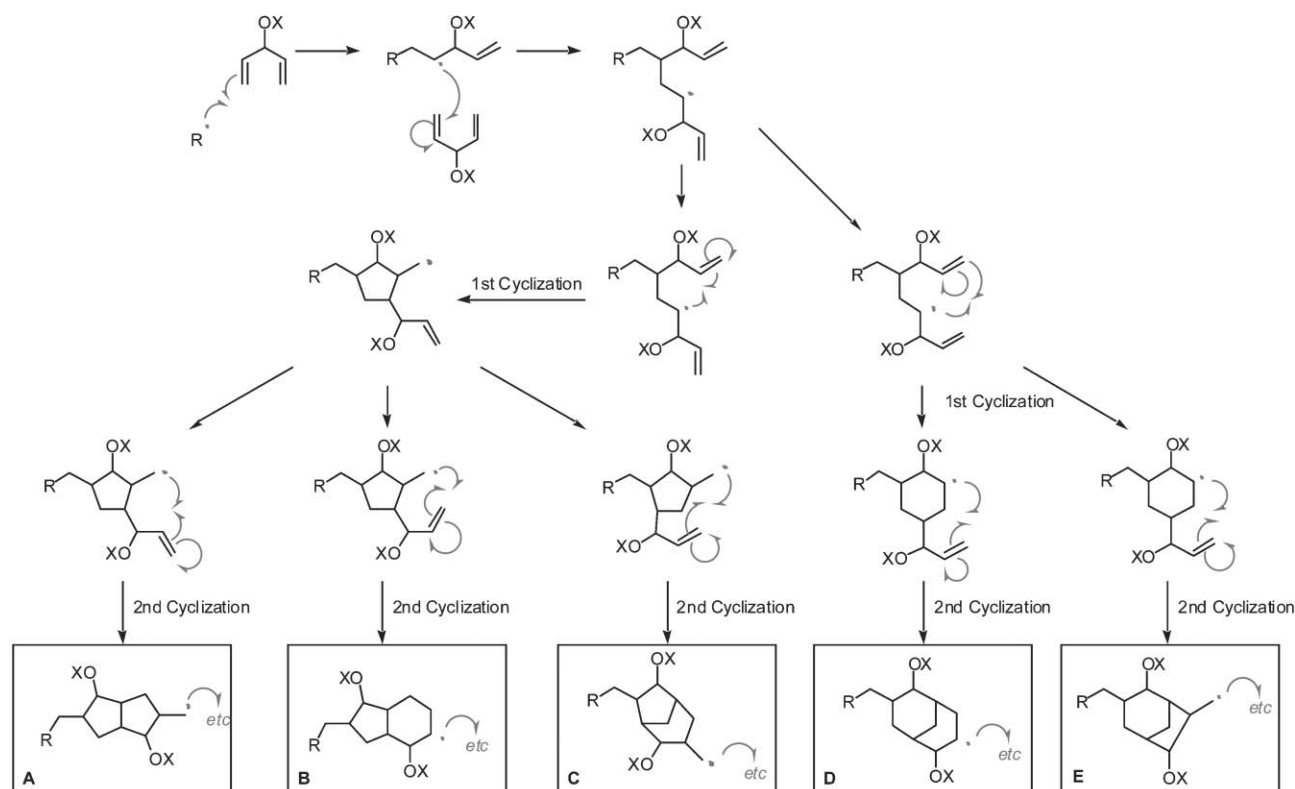
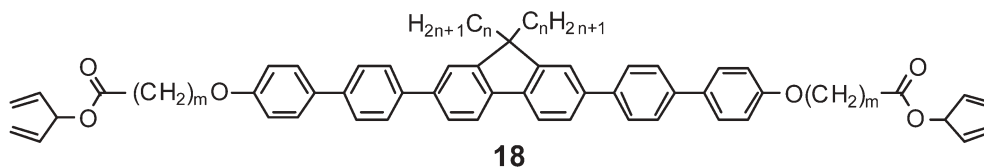


Fig. 8 The initiation process and propagation of the photocyclization reaction of substituted dienes with five atom centres.



present, plus cross-linking between adjacent polymer chains. Consequently, we might expect such systems to be relatively disordered, which is in stark contrast to the over-simplistic view reported by O'Neill *et al.* where electroluminescent networks based on 5-atom centre *reactive mesogens*, see **18** for example, are shown as having only products derived from structure **A**, depicted in Fig. 8.<sup>14</sup> Moreover, in this work polymerization was effected *via* the use of a high power laser without the presence of a photoinitiator. Such autopolymerization for five centre diene systems is highly unlikely because of their generally low reactivity. This suggests that breakdown of the monomeric species occurs first, thereby generating the necessary free radicals for polymerization to occur. Indeed the slowness of the polymerization process in this case was suggested to be an advantage in the subsequent alignment and fixation of the mesogenic units.

It is thus important to fully understand the complexity of the mechanisms that are taking place in the cyclopolymerization processes because they undoubtedly affect the physical properties and the commercial value of the polymers or networks that are created.

### 3. Material processing and polymer properties

#### 3.1 Flow properties of the monomers

In order to examine the flow properties of monomers based on diallylammonium salts and diallylamides, we evaluated viscosities, at 30 °C, for a number of materials possessing two

polymerizable groups and a bridging unit. The bulky polymerizable groups tended to produce monomers with a lower viscosity than the expected value for the bridging group alone. However, the viscosities of the monomer systems tended to rise substantially, as a function of the number of methylene units, in simple systems possessing aliphatic bridging groups. The viscosities (cP) of some of examples are shown in Table 1.

The quaternary salts, which carry a formal charge, are obviously of higher viscosity in direct comparison to their amide analogues. However, by careful choice of the bridging group and the polymerizable moieties, and through producing mixtures of monomers, the viscosity can be tailored to the

Table 1 Example monomer viscosities at 30 °C

Monomer	Viscosity/cP
	1114
	75
	300

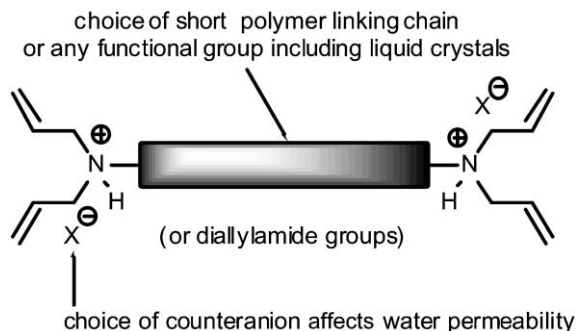


Fig. 9 Generic structure of dimeric diallylamine for polymerization.

application, without the need for solvents. For example, for a wide variety of quaternary salts that were evaluated, the viscosity was found to range from 2.5 cP to 1100 cP. Such monomer systems therefore could be termed “*photopolymerizable ionic fluids*”.

Due to the domination of the monomer properties by the polymerizable units, monomers with very different bridging groups can be mixed to provide homogeneous systems which exhibit little or no microphase segregation, even on curing. This result indicates that the polymer system is extremely flexible in relation to potential applications and offers a simple way to provide adhesion between heterogeneous surfaces, for example.

### 3.2 Coatings for metal and wood surfaces

As noted above, the diallylammonium salts and diallylamides are versatile materials for use in a variety of applications. For example, without optimization or formulation of the materials we have prepared, we have successfully coated wood, stainless steel, aluminium, glass, various plastics and ceramics to form in each case a clear robust coating. As adhesives we have bonded glass to glass, various plastics, including polypropylene, to metals and other plastics. The material properties can also be varied by copolymerization, including the use of plasticizers, branched or straight chain, and cross linkers containing three or more polymerizable diallylamine derivatized groups.

In order to develop materials suitable as coating agents and adhesives, and to overcome the problem of the low degree of polymerization (DP), we focused on a range of difunctional compounds with polymerizable diallylammonium salts or diallylamide groups at each end of the system, as shown in Fig. 9. As these materials form three-dimensional polymer networks, we rationalized that the networks might possess exceptional physical properties.

For the functional systems, we found that the bridging unit located between the polymerizable end groups (Fig. 9) can markedly influence the material properties of the polymer coating or adhesive that is produced. We examined materials which incorporate, for example, bridging groups such as polyamide, polyurethane, polyether, polytetrafluoroethylene (PTFE), polyvinyl and liquid crystal units to mention but a few. For the most part the difunctional-compounds were designed to be oils which could be applied solvent-free to a surface with a brush or a spray. For preparation and testing of the adhesive properties of the materials, the liquid monomers were irradiated between glass plates.

With polymerizable ionic fluid diallyl ammonium salts, the material properties were varied by the use of different counter-anions (see Fig. 10 and general structure **19**), in particular the control of water permeability. For example, the addition of a  $\text{PF}_6^-$  counter-ion confers hydrophobicity to a resultant polymer coating with total impermeability to water, whereas a chloride counter-ion produces a hydrophilic coating which is completely permeable to water, see Fig. 10. Other counter-ions,

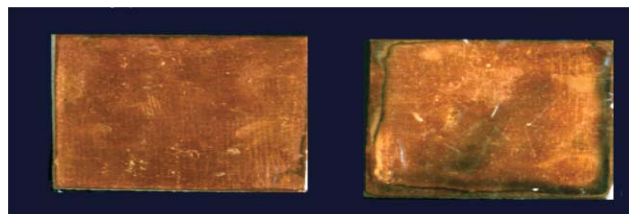
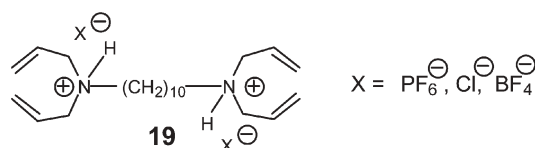


Fig. 10 The plate on the left is coated with a monomer containing a  $\text{PF}_6^-$  counter-ion, this renders the coating impervious to water vapour. The plate on the right is coated with the same diallylamine monomer, but with a  $\text{Cl}^-$  counter-ion. This material allows the passage of water vapour, and hence areas of oxidation can be observed under the film. However, of greater interest is the adhesion offered by these systems. As the diallylamine units possess a full formal charge, the polymers interact well with metallic substrates and provide excellent adhesion.

for example  $\text{BF}_4^-$  show permeability intermediate between these two extremes.



The quaternary systems were also found to bind particularly well with metallic substrates, easily passing the “sellotape test”, and thereby offering excellent adhesion to metal. Indeed, when thin coated metal substrates were flexed little or no breakage or flaking of the coating was observed, unlike acrylates and methacrylates with directly comparable structures that we tested which tended to flake. For example, Fig. 11 illustrates the performance of two coatings on a flexed sheet of stainless steel.

### 3.3 Shear strength, surface energy and impact tests

We examined the shear strength and impact properties of a variety of the polymers and polymer networks that were prepared. The impact properties of the materials were evaluated using an Avery Izod Impact Tester, type 6702 with  $1 \text{ ft lb}^{-1}$  capacity.<sup>15</sup> The tests were carried out by first coating a piece of Teflon, which had been made to a specific size corresponding to the British Standard. The coated Teflon block was then placed into the Impact Tester, and hit with the bar. The result in  $\text{ft lb}^{-1}$  for the fractures was then converted into  $\text{kJ m}^{-2}$ . Shear

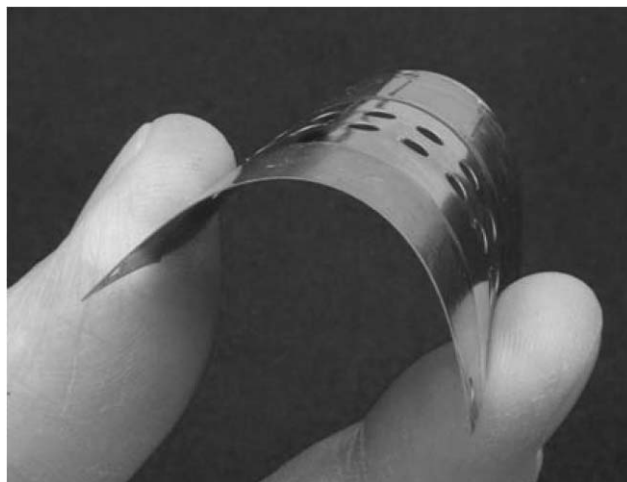
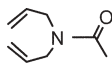
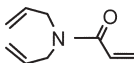
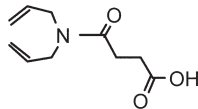
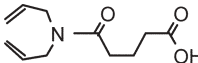
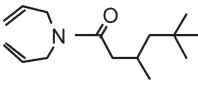
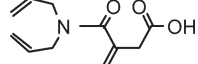
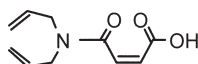
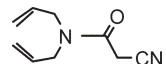
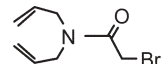
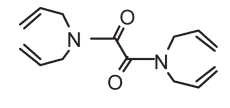
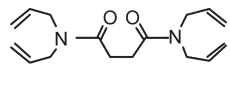
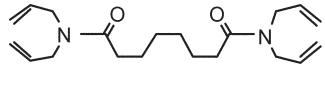
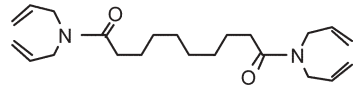


Fig. 11 Flexibility and adhesion of coatings on a flexed metal substrate.



**Table 2** Measured surface energies ( $\text{mJ m}^{-2}$ ) and shear strengths (N) for the polymers prepared as thin films on glass substrates. Izod impact measurements ( $\text{kJ m}^{-2}$ ) for the polymers prepared as thin films on Teflon substrate

Compd no.	Structure	Surface energy/ $\text{mJ m}^{-2}$	Shear strength/N	Izod impact/ $\text{kJ m}^{-2}$
20		57	622 Glass broke	5.42
21		39	622 Glass broke	5.39
22		49	620	5.39
23		50	622 Glass broke	5.46
24		45	622 Glass broke	5.16
25		47	34	5.13
26		42	622 Glass broke	5.52
27		53	622 Glass broke	5.49
28		57	622 Glass broke	5.52
29		72	622 Glass broke	5.46
30		63	600	5.46
31		56	622 Glass broke	5.62
32		53	622 Glass broke	5.65

strengths were measured by first sandwiching the monomers between glass slides and subjecting them to photopolymerization. The shear tests on the resulting glass-polymer composites were carried out using a Hounsfield Tensometer (serial number W5630) and Hoover Mk IV Motor for Hounsfield to BS 170.<sup>16</sup> In many cases the glass slide fractured before the bond was broken. The results obtained for the impact and shear tests (N) are given in Table 2.

The surface energies of the coatings prepared from the polymerization of the materials were measured using a Kruss G23 Contact Angle device. Thus for each polymer, a glass microscope slide was coated with a monomer which was then subjected to polymerization. The resultant polymer coating had five different solvents, of varying polarity, dropped onto it. The contact angle each solvent made with the surface of the polymer was then determined. The angles were then computed to give the surface energy of the polymer, using a program based on Owen and Wendt theory.<sup>17</sup>

In comparison with our un-optimized materials, Table 3

shows the literature values of the surface energy for a number of commercial polymers of similar structure to those tested.<sup>18</sup> Table 4 shows the shear strength of commercially available

**Table 3** Literature surface energies ( $\text{mJ m}^{-2}$ ) for various common polymers

Polymer	Surface energy/ $\text{mJ m}^{-2}$
Polypropylene	29–31
Polyethylene	30–31
PET	41–44
Polycarbonate	46
Fluorinated ethylene propylene	18–22
Polyvinyl fluoride	28
Nylon 11	33
Nylon 6	42
Nylon 6/6	46
Polymethylmethacrylate	39
Polyamide	46
Epoxy resin	47

**Table 4** Measured shear strength (N) for commercial 'Super Glue'

Commercial Glue	Shear strength/N
'Super Glue'	547

**Table 5** Measured Izod impact ( $\text{kJ m}^{-2}$ ) for Teflon substrate

Polymer	Izod impact/ $\text{kJ m}^{-2}$
Teflon substrate (uncoated standard)	5.06

'Super Glue' as determined using identical experimental procedures and Table 5 shows the Izod Impact test result of the Teflon substrate with no polymer coating.

It can be seen from these studies that the polymer networks based on diallylamide substrates have surface energies that are generally greater than standard commercial polycarbonates, and adhesion and shear strength in relation to glass that is somewhat greater than that of 'Super Glue'. In addition, impact testing shows that the polymer networks are stronger than the Teflon substrates used in the tests. Furthermore the networks based on 'diallylamides' are resistant to many chemicals, and they are odourless and colourless.

#### 4. Conclusions

We have shown that 5-, 6- and 7-centred substituted Hall–Goodby dienes can be cyclopolymerized in sunlight or by the use of a low-power UVA sunlamp with a broad spectral range (320–400 nm) to give useful and fascinating alicyclic polymer networks. Unless activated by suitable electron withdrawing groups the cyclopolymerization is often slow and incomplete. However, when suitably activated the polymerization rates can approach those for acrylates. In particular diallylamine, its quaternary salts and diallylamide, can be subjected to fairly rapid photocyclopolymerization to give robust coatings and adhesives. In addition some of the quaternary salts of substituted diallylamines are liquids, thereby providing us with unique examples of photopolymerizable ionic liquids. These discoveries augment, and give a different dimension to, the acrylate and methacrylate monomer and polymer systems that are already commercially available.

#### Acknowledgements

We would like to acknowledge the expertise and contribution made to this work by Dr J. Clint of the University of Hull in the determination of the surface energies of the polymers. We also wish to thank MoD for financial support and Mr A. R. Godber for the kind gift of an impact tester and a shear tester. Development of materials is currently being carried out by Novel Polymer Solutions Ltd, Malvern, Worcestershire, as licence holders of patented material described in this article. Published with permission of the controller, HMSO.

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