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"ENABLING TECHNOLOGY" POLYMERS

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ABSTRACT

An area of polymer science that is of current and growing industrial importance is where the polymer is the enabling technology that makes a component, system, or process work. Without the special polymer, the technology simply does not operate in a useful manner.

The characteristics of this arena are very different from high volume commodity or engineering polymers. Performance is the overwhelming concern and the material is likely to be highly specialized to achieve optimum performance. Cost is of minor concern because the material is used in small quantities and the value it adds to the end use is exceedingly high. Supply is an issue because even at ultra-high prices the sales dollars generated are too small to be of interest to a large polymer producer. In addition, these polymers are often developed by an end-user company which is not in the business of producing polymers and not eager to share the end-use value with a partner.

One of the industrially important examples of polymers as enabling technology, is photoresists used in semiconductor chip manufacture. Within Raychem examples include: acrylic backbone polymers with crystallizable side chains; conductive, crystalline polymer composites; polymer-dispersed liquid crystal compositions; cross-linked fluorinated aromatic polymides or polyethers which will be discussed in detail.

PRESENTATION

For the past 30 plus years, I've been immersed in the industrial side of polymer science and technology. Initially, it was as a researcher and later as a manager and technology leader. However, it is only within the past few years that I have begun to truly understand and appreciate the full scope of polymer science and technology. When you are involved in a business that produces large volumes of polymers, in my case General Electric's Plastics business, it seems logical to equate pounds with commercial importance. However, in my current position at Raychem, a company that tailors and designs polymers for use in electrical and electronic devices and systems, and that is located on the edge of Silicon Valley, I see a very different perspective on the value of polymers. It is easy to grasp the importance of materials produced in million or billion pound quantities; however, it is far more difficult to recognize the importance of specialized materials that may be produced in only a few thousands of pounds.

In this paper, I will detail some thoughts and examples where polymers are the enabling technology that make a device or system work. They contribute enormous value in the end use application even though their quantities are small. My message is that there is more to life as a polymer scientist than rail car quantities of polymers.

At one extreme -- in polymer and polymer-related industries -- are the commodity polymers produced in billions and tens of billions of pounds and sold at prices below and just above a dollar per pound (Figure 1). At the complete opposite end of the scale are what I have termed the "enabling technology polymers" that may cost several hundred or several thousand dollars per pound to produce, let alone sell at a profit. Their total annual usage may be a few thousand pounds and be measured in grams used per individual device. However, the devices may have markets in the tens and hundreds of millions of dollars and without the specialized polymer, they simply don't work. The relative importance of cost and performance varies widely across the spectrum of polymers (Figure 2). In the commodity arena, cost is of predominant importance and performance a lesser priority. In the engineering and specialty polymer arena, the priority is shifted toward performance. In the enabling technology polymer arena performance is virtually all that matters and cost of incidental importance. A further area of contrast is in the business characteristics of these designer materials which are very different from commodity, engineering, and specialty polymers (Figure 3). All of these latter materials have

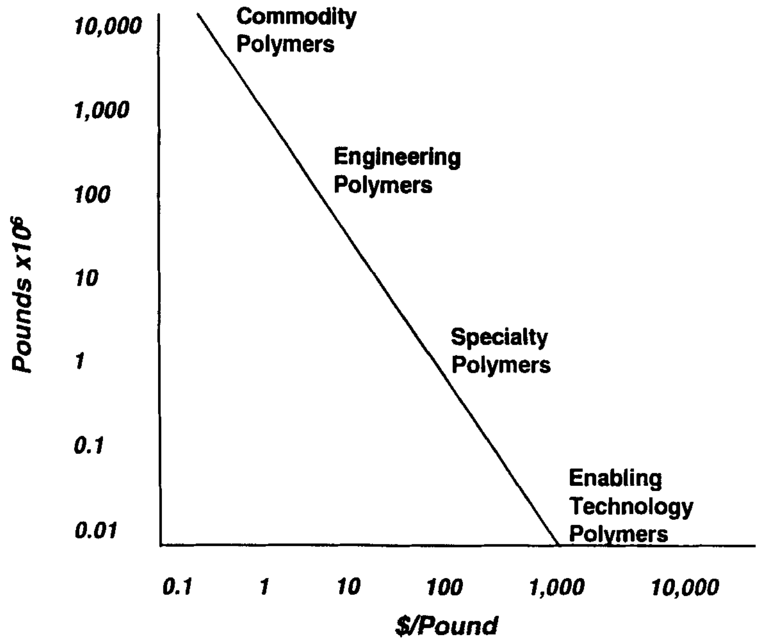


Figure 1. Polymer Price vs. Volume

Commodity Polymers	*Engineering Polymers*
Cost more important than performance	*Cost / performance balance*
Specialty Polymers	*"Enabling Technology" Polymers*
Performance more important than cost	*Performance all that matters*

Figure 2. Polymer Value Spectrum

high capital intensity but offer significant profit-making opportunities in terms of absolute dollar quantities. To participate in these businesses a company must be capable of and willing to invest tens or hundreds of millions of dollars. In contrast, enabling technology polymers can be produced in relatively low investment facilities that are small and highly flexible. The problem arises from the fact that it is difficult to generate interesting quantities of profit dollars by producing and selling a few thousand pounds of a very high price high profit margin material. A large polymer producer has better ways to utilize scarce technical resources.

Profit Potential \ Capital Intensity	Low	Medium	High
High			Engineering Polymers Commodity Polymers
Medium		Specialty Polymers	
Low	Enabling Technology Polymers		

Figure 3. Business Characteristics

Alternative	Impact
• End-user produces the polymer	• Technology retained as proprietary property of end-user • Diversion from mainstream of end-user's business
• End-user outsources production to small custom synthesis company	• End-user must share polymer technology with supplier and risk loss of proprietary property • Reduced end-user flexibility to modify technology
• Polymer producer negotiates deal with end-user to share in value contributed to end-user application	• Very difficult to assign value that is acceptable to both sides

Figure 4. Potential Answers to Dilemma

Fortunately, there are answers to this business dilemma (Figure 4). One is for the end-user to produce the polymer in-house. This approach has the advantage of keeping the technology as proprietary information and making it easy to change as technology and end-use products evolve. The negative side of this approach is that polymer production is diversionary since the mainstream business is producing and selling devices. Also, since polymer production is not a core competence, there is a risk of environmental issues that may become out of proportion to the amount of material involved and that the company lacks the expertise to handle. This is the Raychem answer to the dilemma. We produce a number of very specialized polymers solely for internal use in our products and retain intellectual property and production know-how as proprietary information. We have learned how to deal with environmental issues.

A second option is to out source production to a smaller company that is engaged in custom synthesis. The end-user will have to supply significant knowledge, know-how, and technical support for this to work successfully. Despite confidentiality agreements, there is always a risk of the supplier using the technology to generate additional business or inadvertently leaking proprietary information to a competitor. In addition, it's harder to make changes than if you have complete in-house control of facilities, schedules, and technology.

The third option involves a polymer producer sharing with the end-user in the value of the material. This approach always sounds attractive because the people with the best capability to develop and produce the material are doing what they do best and the end-user is engaged in what it does best, i.e. incorporating the materials into a product. The difficulty arises in reaching agreement on the value contributed by the material to the end-use product. Sharing a significant portion of profit with the material supplier is a difficult obstacle for an end-user company to overcome. I have seen very few examples where this approach has been successful. It still sounds like the most rational approach despite its limited success.

Turning from business issues to technology, enabling technology polymers are nearly always combined with other technologies to produce a final product (Figure 5). The combination of polymer science and technology with other disciplines such as electronics, optics, biology, and medicine is essential. I believe that much of the future scientific excitement and commercial opportunity will arise by combining polymer science and technology with these other areas. The challenge for the polymer end-user is to gain access to these areas in the most effective ways. Having all the capabilities in-house is becoming increasingly unrealistic and various alliances are the obvious answers.

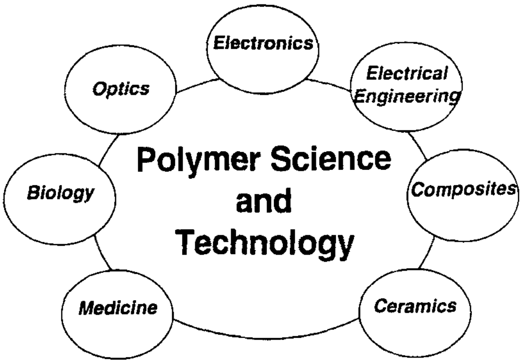


Figure 5. Action at the Interfaces

Key Application Areas

Medical

- Quickly applied and removed casts for broken bones
- Easily removable wound protection
- Polymer drug delivery systems
- Implantable polymers to control "dry eye"

Electronics

- Photoresists
- Polymer dispersed liquid crystal compositions
- Polymer dielectrics for high density interconnects

Figure 6. Enabling Technology Polymers

In thinking of application areas which best illustrate uses for enabling technology polymers, two come immediately to mind - medical and electronics (Figure 6). In the medical area, for example, a family of polymers with acrylic backbones and crystallizable side chains undergoes dramatic changes in some properties when the side chains melt but retain mechanical integrity from the polymer backbone. Permeability, adhesion, and modulus are properties which change by orders of magnitude when the side chains melt. Melting points are tunable over a wide range of temperatures, including body temperature, by changing the side chains. Pre-formed casts that are slipped over a broken wrist or arm, softened by a hair dryer, and shrunk to fit in a few minutes, are one application for these materials. Bandages or surgical blankets which will adhere to skin at body temperature -- and then lose all adhesion by gentle warming or cooling -- are another example. Drug delivery systems that respond dramatically to temperature changes, are a third. Polymers that soften just above body temperature and can be implanted in a tear duct to control the condition known as "dry eye" and later removed if needed, are an additional example. This family of polymers was originally developed in Raychem's laboratories and then spun-off into a separate company, Landec, that is pursuing medical, agricultural, and food packaging applications.

In electronics and semiconductors, the increasing amount of circuitry that can be applied to a silicon chip could not have happened without significant improvements in photoresists. Continued progress in making even more powerful ICs will require continuous enhancement of photoresist technology. In Raychem laboratories for many years, we have been developing polymer-dispersed liquid crystal compositions, known as NCAP, for both active matrix and passive matrix displays. The passive matrix displays are used in applications such as microwave ovens, washers, and copy machines. Active matrix displays combine polymer-dispersed liquid crystal compositions with state-of-the-art electronics for applications such as video projectors that can be viewed in bright room lighting. In these compositions, micron-sized droplets are dispersed in a complex polymer matrix that contains a series of specialized polymers which control switching voltages and coating characteristics when the materials are applied in thin films on a substrate such as glass. Without these specialized polymers, the system is not commercially viable. Another enabling technology polymer activity for Raychem has been in developing polymer dielectrics for high density interconnects which are also known as multichip modules. This is an area that I will discuss in some detail.

First, what is a high density interconnect? The answer is - it is a hybrid between a circuit board and an integrated circuit (Figure 7). It is a way of dramatically increasing the density of circuitry per unit area with short path lengths and resulting high speeds. An HDI is built up from a ceramic or silicon substrate with a series of patterned metal layers separated by polymer dielectric layers, connected by vias and wire bonded to multiple ICs on the top surface. There are many steps in the process with temperatures up to 350°C, repeated solvent exposures, patterning involving aggressive chemical etchants and via formation through laser ablation.

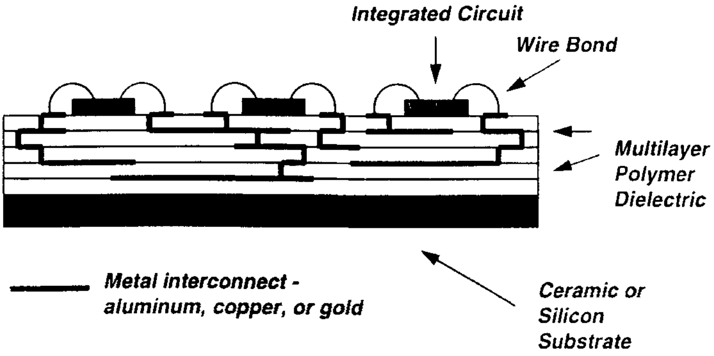


Figure 7. High Density Interconnect

Performance

- Low dielectric constant: less than 3.0
- Low water absorption: less than 1%
- High purity: mobile ions, particles
- Temperature stability: 200°C min. Continuous use
- Thermal transitions: 250°C min.
- Good adhesion: dry and humid
- Mechanical integrity
- Low residual stress

Fabrication

- Thin film forming
- Multilayer construction
- Good planarization
- Good chemical and moisture resistance
- Thermal stability: for processing at 300°C
- Via forming capability
- Processable
- Tuned to process

Figure 8. Polymer Design Parameters

There are a daunting series of design parameters for the polymer dielectric: the dielectric constant should be less than three, water absorption less than 1%, temperature stability of at least 200°C continuous use and above 300°C for short term exposure, mechanical integrity as a thin film and a series of fabrication-related requirements (Figure 8). Particularly critical requirements are moisture absorption and planarization. The former is critical because of the effect moisture absorption has on dielectric constant and the need for stable electrical properties. Also, if a low moisture absorbing polymer can be used, a high temperature bake step to remove

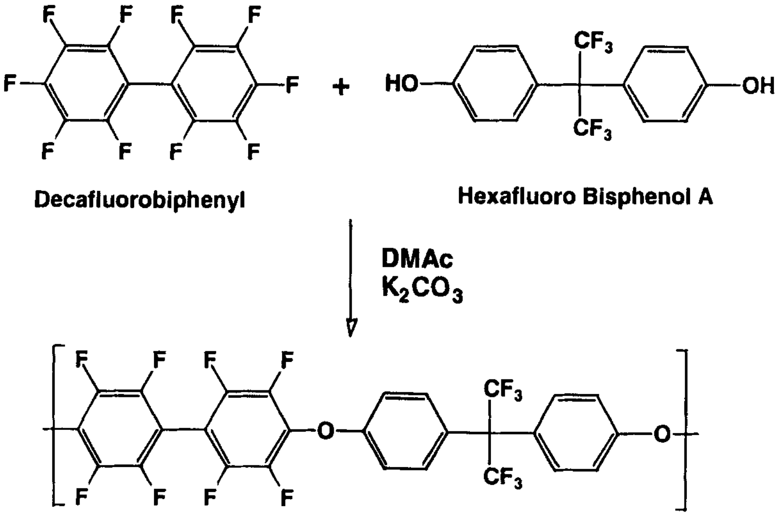


Figure 9. Fluorinated Polyarylethers

traces of water can be eliminated. The latter property of good planarization is critical because of very small features in HDIs and multiple layers that highlight variability in surface smoothness. Aromatic polyimides, the materials most frequently used in these applications, have higher than optimum water absorption arising from polarity of the imide groups. They also do not provide excellent planarization. Use of fluorinated dianhydrides reduces moisture absorption significantly and adding fluorinated diamines leads to further reductions. However, there appears to be a minimum of ~ 0.7% moisture absorption that is not reduced by further fluorination. Because of its business interests in high density interconnects, Raychem established the goal of developing a proprietary material having superior performance in HDI applications.

After investigating a series of polyimides, fluorinated polyimides and other heterocyclic polymers, we focused on fluorinated polyarylethers derived from decafluorobiphenyl, a bisphenol and potassium carbonate in dimethylacetamide (Figure 9). The dielectric constant of the polymer from hexafluoro bisphenol A had a dielectric constant of 2.5, moisture absorption of 0.15% and a Tg of .190°C[1]. We prepared a series of materials, a few of which are shown here, and measured their properties (Table 1). Dielectric constants ranged from 2.5 to 2.8 at 0% RH and from 2.6 to 3.1 at 60% RH. Moisture absorption ranged from 0.1% to 0.5%. Thermogravimetric analysis showed excellent results from several polymers with

TABLE 1. Dialectric Properties and Moisture Absorption of FPAE Polymers

Polymer	Dielectric Constant 0% RH	Dielectric Constant 60% RH	Moisture Absorption (wt.%)
FPAE 1	2.50	2.60	0.10
FPAE 2	2.60	2.70	0.15
FPAE 3	2.60	2.70	0.10
FPAE 4	2.75	3.00	0.45
FPAE 5	2.80	3.10	0.50

Fluorinated Polyarylethers

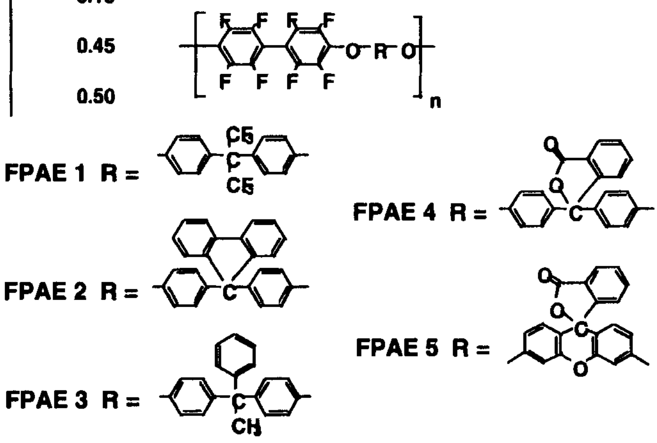


TABLE 2. TGA Analysis of FPAE 1, 2, and 4

Property	FPAE 1	FPAE 2	FPAE 4
TGA Weight Loss			
Onset in Air (°C)	500	500	450
Onset in Nitrogen (°C)	510	540	
Maximum Weight Loss @ 1000°C (%)	60	37.5	98
Isothermal Weight Loss in Air			
3 Hours at 400°C (%)	2.5	2.7	
3 Hours at 450°C (%)	19.8	3.6	50

TABLE 3. Mechanical Properties of FPAE 1 and 2

Property	FPAE 1	FPAE 2
Thermal Coefficient of Expansion (ppm/°C)	76	65
Ultimate Tensile Strength (Kpsi)	8.3	10.7
Elongation at Break (%)	85.0	36.0
Elastic Modulus (Kpsi)	245	295

TABLE 4. Fluorinated Polyarylethers vs. Polyimides

		Fluorinated Polyarylethers	Polyimides	Fluorinated Polyimides
Moisture Absorption		0.1 - 0.5%	~ 3%	0.7 - 1.0%
Dielectric Constant	- 0% RH	2.5 - 2.8%	~ 3.2%	2.7 - 2.9%
	- 60% RH	2.6 - 3.1%	~ 3.7%	3.0 - 3.3%

the best performance from the bisphenol derived from fluorene (Table 2). This material lost only 2.7% of its weight after 3 hours at 400°C in air and only 3.6% after 3 hours at 450°C. Mechanical properties were adequate for the application (Table 3)[1, 2]. Comparing fluorinated polyarylethers with polyimides and fluorinated polyimides, the polyethers showed significantly lower moisture absorption, generally lower dielectric constants and in several instances less change in dielectric constants at 60% RH (Table 4) [1, 2].

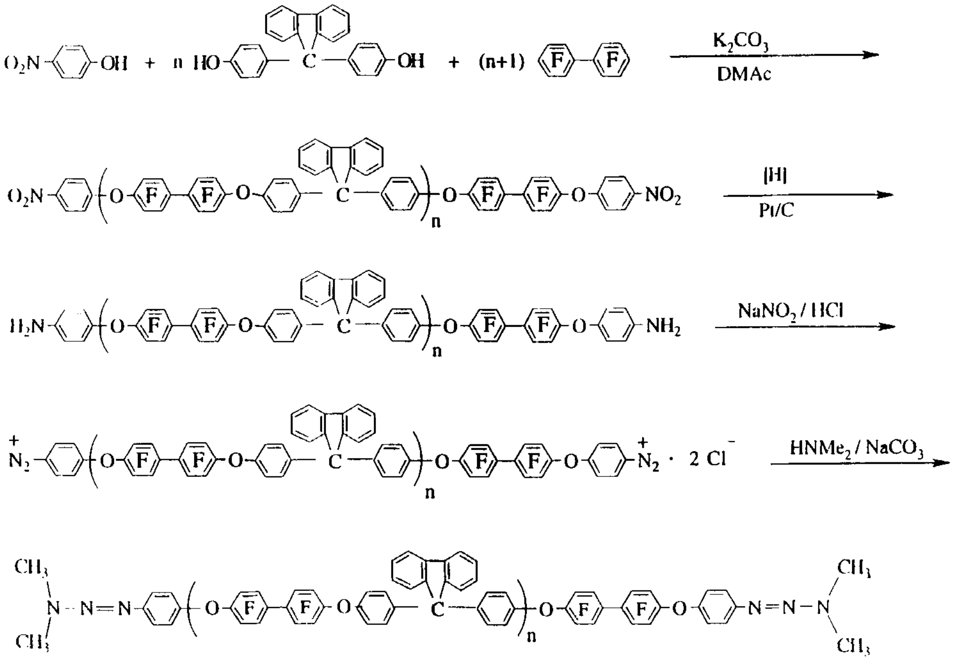


Figure 10. Phenyltriazene End-Capped Oligomer of Fluorinated Aryl Ether

We concluded that the fluorinated polyarylethers demonstrated superior performance in a number of critical design parameters. However, they lack solvent resistance and cannot withstand the conditions of the photoresist development process. We also concluded that we needed to crosslink these materials to attain the required solvent resistance.

The design parameters for crosslinked HDI polymer dielectrics included: solvent resistance under processing conditions, solubility in organic solvents prior to thermal curing, efficient cross-linking under process conditions and minimal degradation of mechanical, electrical and thermal properties.

We explored a number of approaches to cross-linking and found that aromatic triazenes were particularly effective. Based upon literature reports, we presume the mechanism of cross-linking to be triazene decomposition to form aryl radicals which then arylate the polymer chain.

One approach consisted of adding p-nitrophenol as a chain-stopper in the polyether polymerization (Figure 10). Terminal nitro groups were hydrogenated to amines, diazotized and coupled with a secondary amine to produce a series of

TABLE 5. Glass Transition Temperature (Tg), Gel Contents, Dielectric Constants, and Solvent-Induced Crazing of 1 and 2

	1*	2	
Repeat Unit (n)	--	6	20
Tg (°C, DSC)	258	302	288
Gel Content (°C)	0	98	93
Dielectric Constant			
@ 0% RH	2.60	2.70	2.60
@ 60% RH	2.70	2.80	2.70
Solvent-Induced Crazing	Yes	No	No

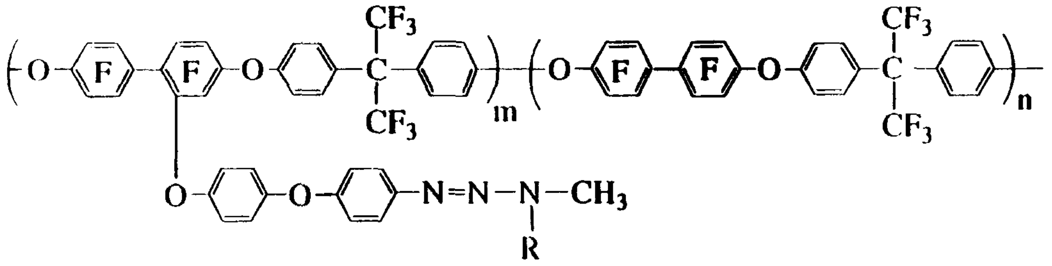
*** Unmodified FPAE**

TABLE 6. TGA Analysis of 1 and 2

	1*	2	
Polymer Repeat Unit (n)	--	6	20
TGA Weight Loss 20°C/min)	562	542	536
Onset in Air (°C0			
Onset in Nitrogen (°C)	558	543	540
Isothermal Weight Loss at 400°C			
3 Hours in Air	4.9%	8.3%	8.5%
3 Hours in Nitrogen	4.9%	9.2%	9.3%

*** Unmodified FPAE**

TABLE 7. Physical Data of Self-Crosslinkable Fluorine-Containing Poly(arylene ethers)s 2 and 3



2 : $R = CH_3$
3 : $R = C_6H_5$

	polymer prior to cure						cured polymer							
								dielectric constant[d]		TGA[e]				
	pendant added[a]	R	n/m[b]	M_n	M_w	T_d[c] (°C)	cure temp (°C)	0% RH	60% RH	onset wt loss (°C)	isothermal wt loss, 3 h at 400 °C (%)	T_g[c] (°C)	gel (%)	stress crazing
1	none (control)	n/a	n/a	22,790	345,550	none	**300**	**2.46**	2.56	517	2.4	189	0	yes
2	0.6	CH_3	3.8	30,620	788,200	283	**300**	**2.56**	2.83	509	2.7	236	99.7	no
3	0.4	C_6H_5	3.9	32,020	1,481,000	208	**215**	**2.65**	2.76	521	5.6	218	98.0	no

a: mmol per g of resin
b: measured by ^{1}H-NMR integration.
c: measured by DSC at 10 °C/min under nitrogen.
d: measured at 10KHz.
e: measured at 10 °C/min in air.

oligomers terminated with triazenes. These materials gave gel contents greater than 90%, did not show solvent-induced crazing as did the base polymer and with an average chain length of 20 repeat units showed no effect on the dielectric constant (Table 5). Although there was an increase in weight loss after 3 hours of 400°C, the percent loss did not constitute a problem (Table 6) [3, 4].

A second approach to a self-crosslinkable polymer is to incorporate the triazene moiety in a pendant side chain. Introduction of the side chain was accomplished through nucleophilic displacement of fluorine with a triazene-containing phenoxide (Table 7). In the two examples shown, gel contents of 98% or greater were achieved with no evidence of solvent-induced stress cracking and minimal changes in dielectric constants. Weight loss was somewhat elevated in one case but not enough to be of concern [5].

Our overall conclusion from this work is that this family of crosslinked polymers does provide the superior performance we were seeking. Their further development and commercial use is being pursued.

In closing, I want to leave you with three messages:

First: Pounds of material produced and sold do not tell the whole story of value and industrial importance. We need to have a broader perspective to comprehend the entire scope of polymer science and technology.

Second: Future opportunities for research in polymer science are greatest at the interface with other disciplines. This is especially true for the enabling technology polymers.

Finally: Polymer science and technology in all its areas is continuing to grow. One only need look at the metallocene catalysts for polyolefins to recognize that there is opportunity even in commodity polymers. Companies that have the vision and patience to continue their investment in polymer science and technology will be the industry leaders in the 21st century.

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