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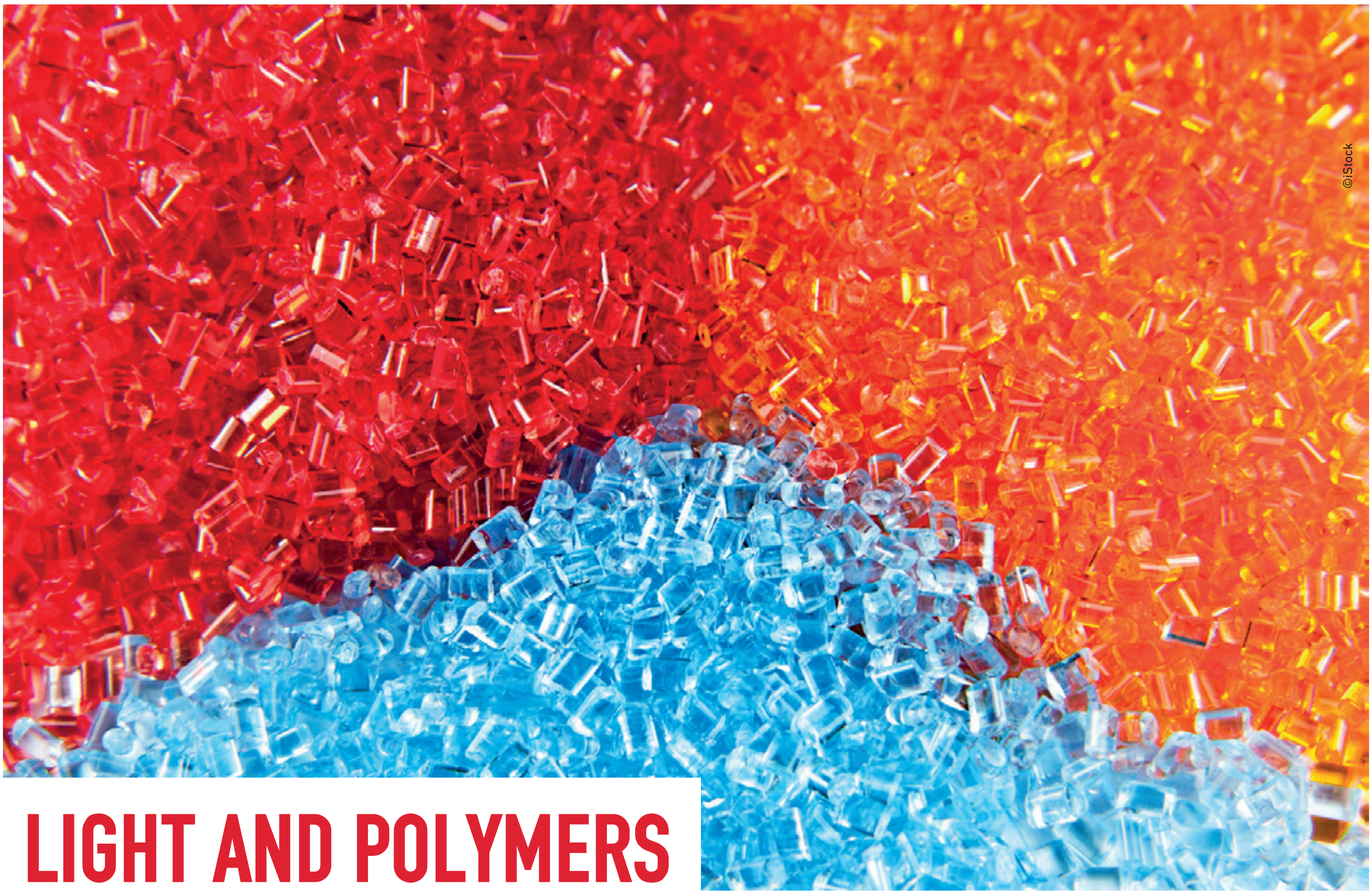

LIGHT AND POLYMERS

Light is the natural source of life and all living organisms on earth need light to survive. The relation between light and life is expressed in the noblest way by the famous philosopher Mevlana Celalettin Rumi [1] with the following words:

Born from the infinite darkness.

Spotted the "light", scared. Cried...

With time, learned to live with the "light".

Spotted the darkness, scared. Cried....

Today, light plays a crucial role in everyday life. Besides lightening, many industrially important applications such as light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), solar cells, and photovoltaics are all related to the use of light. Many chemical reactions can also be triggered by light. The use of light in polymer science dates back to as early as ancient Egyptian times. The so-called mummy is a dead human or an animal body preserved by special techniques and it has become the most famous aspect of the ancient Egyptian period (Figure 1). The dead bodies, after being washed and cleaned, were covered by materials that were immersed in special resins and kept in sunlight. Photochemical curing resulted in the preservation of the bodies in the form of mummies for centuries.

Figure 1. Antique illustration of an Egyptian mummy.

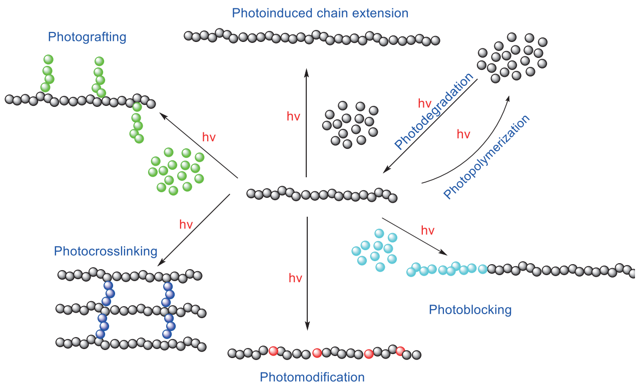

Figure 2. Light-induced synthesis of polymers with various topologies.

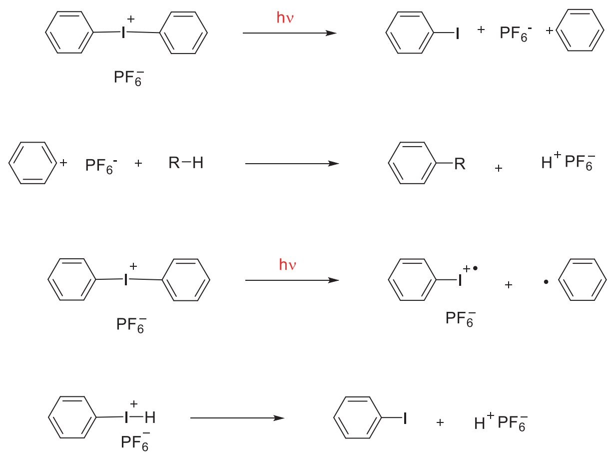

Figure 4. Photoinduced acid generation for cationic polymerization.

Light also plays a predominant role in technical polymer synthesis [2]. Polymers with a wide range of topologies can be synthesized by photochemical means (Figure 2).

Among the various modes of photopolymerization processes, free radical polymerization is in the more advanced state due to its applicability to industrially important vinyl monomers and the availability of a wide range of photoinitiators acting at the whole range of the electromagnetic spectrum. The general radical generation process is based on either α-cleavage or hydrogen abstraction mechanisms (Figure 3).

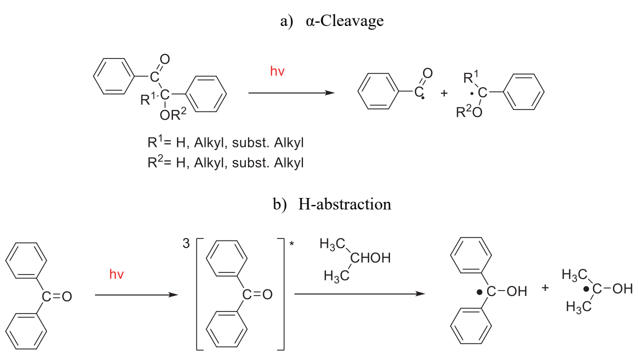

Figure 3. Photoinduced radical generation by α-cleavage (a) and H-abstraction processes.

Photoinitiated cationic polymerization [3] has also become an important process for the curing of epoxy and some vinyl monomers that can be initiated by the photoinduced generation of Brønsted acids (Figure 4). Thus formed photoacids readily react with the monomers to initiate the polymerization. The non-nucleophilic nature of the counter anions, such as PF_6^-, ensures that polymerization proceeds even after the light is turned off.

More recently, we have shown that step-growth polymerization [4] can also be accomplished by photoinduced electron transfer [5] or radical coupling [6] reactions. In all conventional polymerizations due to the various side reactions, molecular weight and functionality are not properly controlled. However, recent studies [7,8] showed that such control can be achieved by photoinitiated living/controlled polymerization methodologies.

Furthermore, photochemical routes provide the possibility to fabricate polymer/metal [9] or clay [10] nanocomposites. Nano-sized metals and their composites play a crucial role in various applications as bio- and optoelectronic materials. Usually, gold and silver nanoparticles and polymers are independently prepared and then their composites are formed. Recently, we have shown [9] that such composites can be obtained directly by simultaneous reduction and polymerization processes by the use of light. The typical photochemical dual process is presented schematically on the example of the gold-poly(ethylene glycol) diacrylate nanocomposite in Figure 5.

To improve the mechanical properties of polymers, the usual strategy is to combine them with naturally abundant materials such as clays. However, clay and polymers are immiscible and when they are mixed phase separation occurs and heterogeneous materials are formed. We have developed [10] a new strategy by inserting photoinitiators between the layers of clay by exchanging sodium ions on the surface (intercalation). Upon irradiation, polymerization starts and the layers are exfoliated, resulting in the formation of homogeneous nanocomposites.

Photoinduced electron transfer reactions can be adapted to

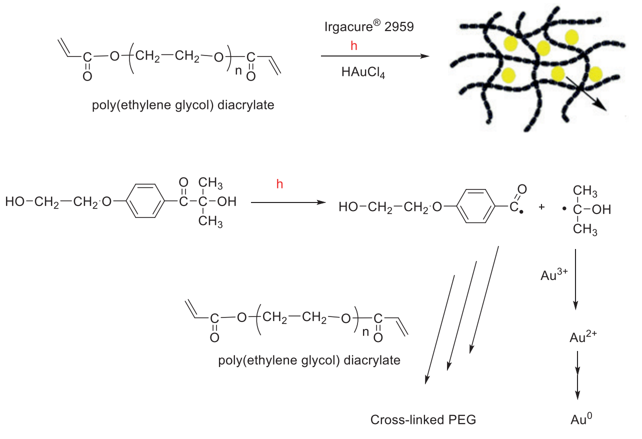

Figure 5. Photoinduced preparation of gold-poly(ethylene glycol) acrylate nanocomposites.

copper-catalyzed cycloaddition reactions known as "click chemistry", which allows simple coupling of small organic compounds and polymers [11] (Figure 6). In this case, the catalyst Cu(I) is produced by the reduction of Cu(II) salt by photochemically generated electron donor radicals.

In conclusion, light-activated processes for the preparation of polymeric materials provide a versatile methodology offering several advantages compared to the thermal analogous technique. These include low energy requirement, spatial and temporal control, and high reaction rates, and therefore light-induced approaches can be considered "green".

Moreover, the possibility of conducting reactions in the UV, visible, and even non-harmful near-infrared [12-14] region of the electromagnetic spectrum provides wavelength flexibility for specific applications.

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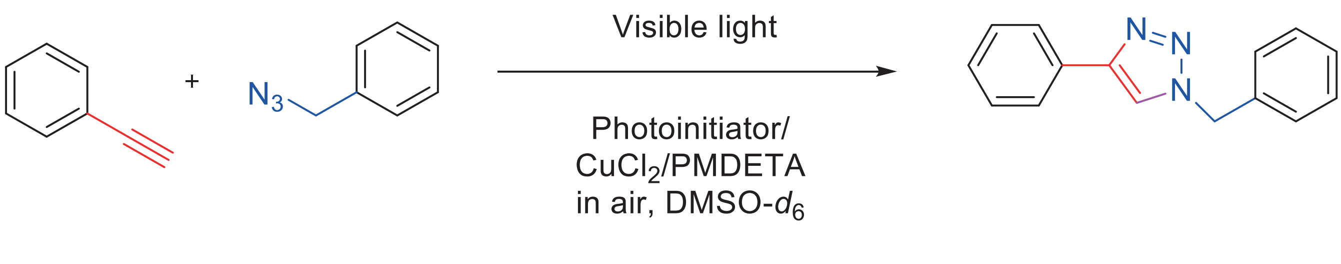
Yusuf Yagci

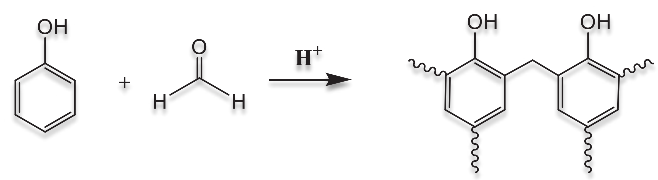


Bakelite bracelets

PHENOL-FORMALDEHYDE MIRACLES

In 1872 Adolph von Baeyer, a German chemist, heated aqueous formaldehyde with phenol to yield a hard, resinous, noncrystalline product. However, the chemistry to elucidate the structure of such materials was not available at that time [1]. This resin protects wooden materials in particular from external factors, such as moisture.

In 1907, Leo Baekeland, a Belgian-American chemist, developed a process via a phenol-formaldehyde reaction to produce a strong and flexible resin, which was marketed under the name "Bakelite". Bakelite, the first plastic material made from synthetic components, has attracted enormous interest since that time. Bakelite is an important synthetic material used especially in electrical devices due to its high resistance to electricity.



An old-time radio and telephones made using Bakelite material

The story of phenol-formaldehyde in the cyclic structure begins with the work by David C. Gutsche. He isolated calixarene, which may be a third-generation compound, from the condensation of phenol and formaldehyde in basic conditions and with procedures that allow their isolation in different ring sizes. Mainly, they contain 4, 6, or 8 phenol residues. The name "calixarene" was originally conceived due to their resemblance to the vase-like shape that these phenol-derived macrocycles assume when they are in the conformation where all aryl groups are oriented in the same direction [1]. Their name derives from the Greek "calix" (meaning "vase") and "arene", which indicates the presence of aryl residues in the macrocyclic structure.

The de-alkylation reaction can be carried out quite effectively by a reverse Friedel–Crafts process, using a Lewis acid as catalyst ($AlCl_3$). Thus this reaction allows us to remove the tert-butyl groups and to make the p-position of phenolic units undergo further modifications with different groups. Some of the main characteristics that make calixarenes interesting for various types of applications are that they are not expensive materials, they are well-defined oligomers, they can be prepared with different sizes of cavities, they can be easily functionalized inserting even quite different groups, they show exceptionally high and selective complexation capacity of metal ions and molecules, and they show remarkably high chemical and thermal stability [2].

Their possible applications range from nanomedicine to biochemical and material science. For instance, patents were filed that claim the use of calixarenes in cosmetic and pharmaceutical formulation, cell transfection, and antibacterial agents. They have also been proposed as dental materials, adhesion promoters, hair dyes, photographic toners, glass photoresists, and antioxidants [3,4].

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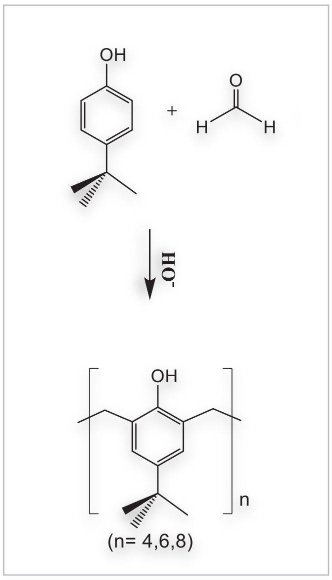
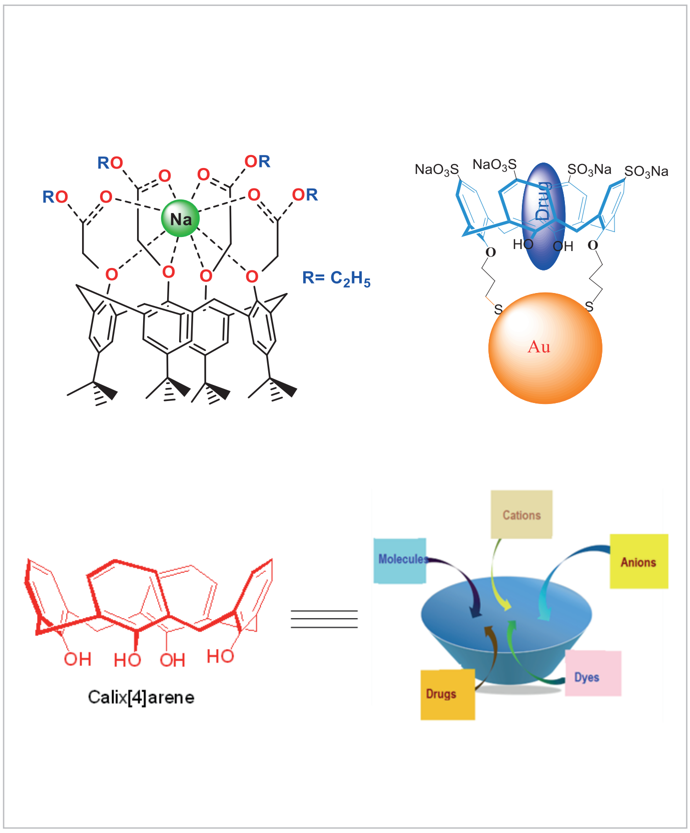
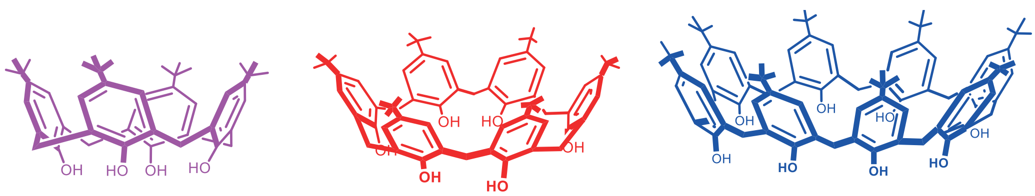
Mustafa Yılmaz



David C. Gutsche and coworkers reported an easily reproduced procedure for synthesizing p-tert-butylcalix[4]arene, p-tert-butylcalix[6]arene, and p-tert-butylcalix[8]arene in good or excellent yield on any scale from a gram or less to many kilograms.





BIRTH OF ELEMENTS AND THE ATOM

PLATON ARISTOTELES

Hellenic statues of Plato and Aristotle ancient Greek philosophers and scientists

The concepts of elements and the atom are of Greek origin. Of course, the Greeks did not consider them as we do today. In Ancient Greece, although Empedocles believed that all materials were made of four primary substances: earth, air, fire, and water, the term element was introduced by Plato. It was thought that the appearance of a material could be explained by the combination or separation of these elements through the influence of love (attraction) and hate (repulsion).

Plato, adopting Empedocles' theory of elements, thought that geometry was the best way of thinking about nature and explained the smallest part of fire (not an atom as he did not believe in atoms) in the shape of a tetrahedron, air as an octahedron, water as an icosahedron, and earth as a cube.

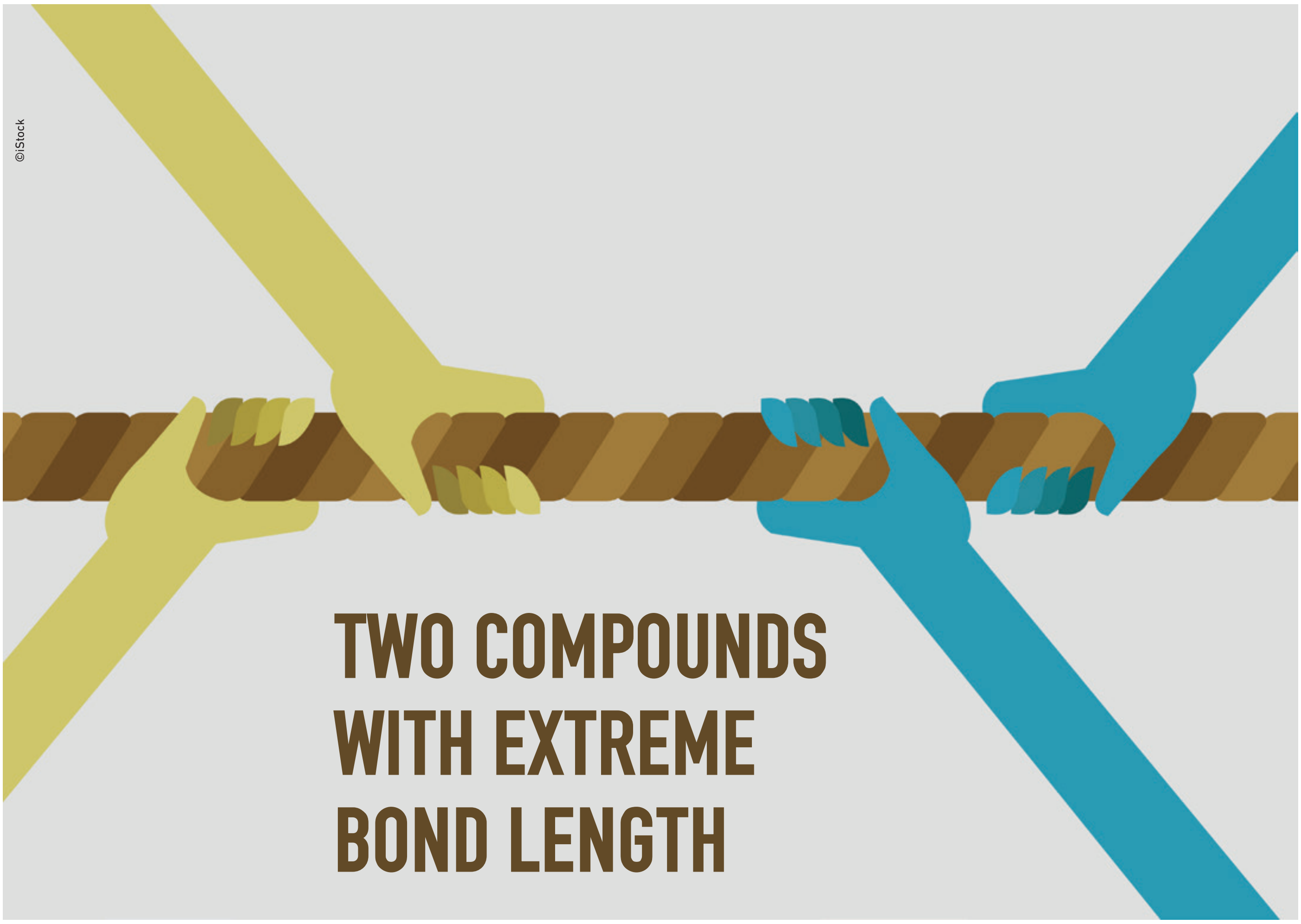
Aristotle also accepted the theory of four elements, but not in the way Empedocles claimed that the elements were immutable and the materials differ only in their compositions. On the other hand, Aristotle thought that the elements change when they combine. Moreover, Aristotle explained that elements had qualities based on how we experience them: hot, cold, dry, and moist. He said that each element was endowed with two of the qualities; thus, earth was dry and cold, water moist and cold, air moist and hot, and fire hot and dry. An element could be turned into another by changing one or two of its qualities, such as earth could turn into water by changing its dryness to moistness.

Both Plato and Aristo did not accept the theory of the atom claimed by atomists, i.e. Leucippus and Democritus.

The idea of the atom as the smallest and indivisible entity is one of the oldest concepts in science. It had its origin as a philosophical problem that Greeks discussed for a long time. Heraclitus said that *change* is the basic nature of all things. On the other hand, Parmenides did not agree with Heraclitus and said that reality is unchangeable and change is only an illusion. Democritus (probably Leuccipus was the father of atomic theory, but little known about him) explained that the change was the local motions of parts that in themselves were unchangeable and invisible. Those parts were atoms, which comprised all being; everything else was void. He claimed that materials differ from each other as a result of the shapes, positions, and grouping of the constituting atoms. He also said that while in solid bodies the atoms stick together, in liquids and gases atoms do not stick together and rebound from one another in different directions. Denser bodies are made of bigger atoms (but still indivisible). He stated that there was no limit to the size of atoms. They could be as big as a world could exist somewhere.

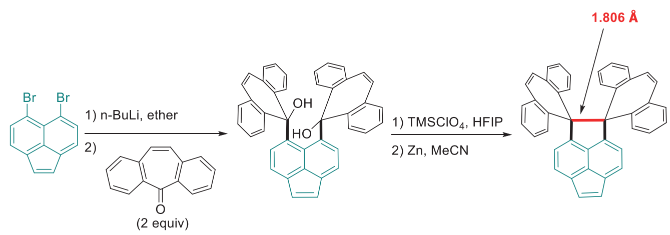
Atomists did not have many followers until the 17^{th} century. Even Dante allocated him a very low place in hell.

Turan Öztürk

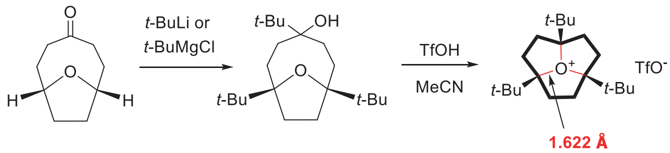


TWO COMPOUNDS WITH EXTREME BOND LENGTH

In 2018, one of the longest C_{sp3}–C_{sp3} bond lengths to date in highly strained hydrocarbons was reported by Ishigaki et al. from Hokkaido University, Japan [1]. The C–C covalent bond length (1.806 Å) of this highly strained core-shell-type hydrocarbon is 1.17 times greater than the standard length (1.54 Å). This hydrocarbon was prepared from dibromoacenaphthylene and dibenzosuberenone in two steps. Firstly, the corresponding diol was obtained by lithiation of 5,6-dibromoacenaphthylene followed by the addition of dibenzosuberenone. After the diol was exposed to acidic conditions in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), the resulting precursor dication was reduced with Zn powder to yield this extreme compound as an orange crystal.



In 2012, stretching of a C–O bond to a record length was reported by Mascal and coworkers [2]. The team observed the formation of unusually long C–O bonds during the building of oxatriquinane structures. The substitution of the oxatriquinane ring system with *tert*-butyl alkyl groups resulted in an extraordinary C–O bond of 1.622 Å in 1,4,7 tri-*tert*-butyloxatriquinane.



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Nurullah Saraçoğlu

Olive oil on a wooden table

A DELICIOUS AND VALUABLE GIFT FROM THE UNDYING TREE: VIRGIN OLIVE OIL

The symbolic plants of the Mediterranean civilization are figs, grapes, wheat, and olive trees. The olive tree is a very long-lived plant. It is the rich tree of poor soils. The Minoan people of ancient Crete, ancient Egyptians, Phoenicians, ancient Greeks and Romans, Berbers, and later Muslims in the Middle Ages contributed greatly to olive cultivation in the Mediterranean basin [1]. Turkey is the fourth largest producer of olive oil in the world. Ninety-one domestic cultivars of olives (89 domestic cultivars + 2 hybrid olives) are officially registered in Turkey. The economically important domestic cultivars are the following: Memecik (South Aegean district, oily cultivar, approximately half of the country's olive presence, having geographical registration certificate), Ayvalık (North Aegean [Edremit Bay] district, oily, having geographical registration certificate), and Gemlik (Marmara region [Gemlik Gulf – Bursa] district, table + oily, having geographical registration document). Olive fruit cannot be consumed directly because it contains oleuropein, an especially bitter phenolic component. It is considered a processed fruit (table olives) as a result of some processes. Only the oil with natural properties is obtained from the olive fruit with the help of physical methods (pressing, centrifugation, and percolation). Virgin olive oil, called liquid gold, is a fruit oil or an oily juice [2-4].

In the evaluation of virgin olive oil, its sensory qualities come before its analytical qualities. Although the analytical quality values of many virgin olive oils on the market are appropriate, their sensory quality criteria (sensory defects) may be insufficient. The quality of natural olive oil starts with the harvest. Olive fruit is very sensitive to damage. Harvesting must be done manually or by machine to obtain a ground fruit. It should be transported in plastic containers having ventilation holes. To protect the sensory quality of the oil, the ground/good olives (collected from the branch) and the damaged/bad olives (that have fallen onto the soil) must be processed separately for oil extraction. The oils of good and damaged olives should be stored separately and should not be mixed [2]. From the ancient period up to the 1960s, virgin olive oil was obtained entirely by pressing (classical) methods and today the oils are mostly produced based on centrifugation methods, which are continuous (modern) systems known as 3 (oil + olive pomace + wastewater) phase and 2 (oil + high humidity pomace) phase [3].

Virgin olive oil contains chemically saponified (triglycerides or triacylglycerols and fatty acids known as neutral oil, 98-99%) and non-saponifying components (the most important are sterols, phenolic compounds, volatile aromatic components, and squalene, 1-2%). Fatty acids (as a source of essential fatty acids) are an important food ingredient for human nutrition. The fatty acid profile in virgin olive oil follows as the main major component according to official norms: palmitic (7.5-20 %) and stearic (0.5-5.0%) (saturated fatty acids, [SFA]), oleic acid (55.0-83.0 omega 9, monounsaturated fatty acid, [MUFA], the dominant and characteristic most important fatty acid in olive oil) and linoleic (3.5-21% omega 6), linolenic (<0.9 omega 3). These fatty acids are known as polyunsaturated fatty acids (PUFAs). According to the fatty acid profile, olive oils are classified into two types: 1st type oils, including low linoleic and palmitic and high oleic acid levels (Northern Mediterranean countries [Spain, Italy, Greece, Turkey], and 2nd type oils, containing high linoleic and palmitic acid and low oleic acid contents (North Africa [Morocco, Algeria, Tunisia, and Libya]. The fatty acid profile is a useful marker in determining possible frauds and adulterations in virgin olive oils, and this parameter was successfully used in the characterization and classification of oils based on their cultivar and regional basis [4].

Squalene (200-12,000 mg/kg for virgin olive oil), a component found in a non-saponifying fraction of oils, is an important hydrocarbon specific to this oil. The highest value of squalene in nature is found in the shark liver. Squalene helps regenerate tissue cells (anti-inflammatory) and is a protective (anti-carcinogenic) substance against skin cancer. Other important non-saponifying components in virgin olive oil are biophenolic substances. These components contribute to the formation of permanent sensory taste and unique flavor (fruity, bitter, and pungent) in virgin olive oil and the shelf life (oxidative stability) as a technological property. In addition, phenolic components are a remarkable source of antioxidants (anticarcinogens, inhibitors of free radicals) in human nutrition [4].

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Harun DIRAMAN

Olives on the tree.

Olive tree is the rich tree of poor soils.

Cultural Heritages

Ephesus - Selçuk, Turkey

THE ANCIENT CITY OF EPHESUS

Hüseyin YURTTAŞ , Esra Halıcı, Burak Muhammet GÖKLER, Muhammed Emin DOĞAN

The first establishment of Ephesus, which is a port city in the Selçuk district of İzmir Province, goes back to as far as 6000 BC. The city named Apasas in the second half of the 2nd millennium BC in Hittite documents is located in today's Ephesus region. Especially the finds at Ayasuluk showed that Apasas, the capital of the Arzawa-Mira Kingdom of Hittites in Western Anatolia, is Ayasuluk Hill. The population of Ephesus, where immigrants from Greece lived in 1050 BC, constituted Anatolian peoples such as Carians, Lelegians, and Lydians before the Ionians. The city was moved by the King of Lydia Croesus in 560 BC to around the Temple of Artemis, and then to its present place by Lysimachus, one of the generals of Alexander the Great, in the 300s BC. The city, which was established in the valley between mounts Panayır and Bülbül, is surrounded by a 9-km-long wall. Experiencing the richest period in the Hellenistic and Roman periods, Ephesus was the capital of the Asian Province with a population of 200,000. Due to the filling of the harbor during the Byzantine period, the city was again moved to Ayasuluk Hill, where the first finds were made. The new name of the city, which had started to take shape since the 7th century AD, was Hagios Theologos (holy theologian). With the Turks arrival in the 14th century, the region became known as Ayasuluğ/Ayasuluk. The name of the city, which the Aydinids used as a center for a while, was documented by the Genoese as Alto Luogo. During the Ottoman period, the name Ayasuluk continued to be used and in 1914 it was changed to Selçuk.Ephesus is an important settlement in terms of historical and cultural ruins. The Temple of Artemis

Great theater of Ephesus ancient city in Turkey in the city was built entirely of marble in 550 BC and is one of the Seven Wonders of the Ancient World. Another important building in the region is the Ephesus Theater, which was started to be built in the 1^{st}-2^{nd} century AD with a capacity of 25,000 people. Other important cultural ruins include the Library of Celsus, the upper agora and its basilica, the Odeon (the place seating 1400 people where city council meetings were held), the Prytaneion, the Gate of Hercules, the terrace houses, the Fountain of Trajan, the public baths and latrines, the Octagon burial chamber, the Temple of Hadrian, the Church of Mary, the palace structure, and the Gymnasium.

Amphitheater in Ephesus, Turkey

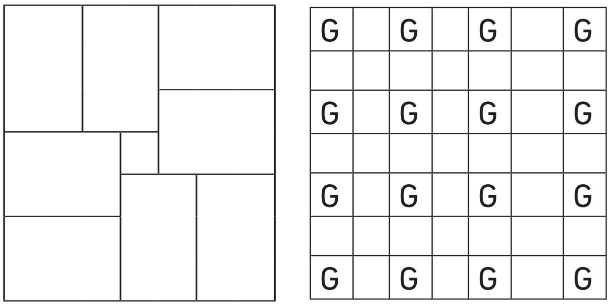
The Library of Celsus, built in AD 135, in the ancient city of Ephesus.

TODAY'S PROBLEM AND YESTERDAY'S ANSWER

Problem 4.

A modern artist uses only 8 colors. It turns out that each of his paintings presented at the exhibition is painted using only 3 colors and any 2 of his paintings have at most 1 common color. What is the maximal possible number of paintings by the modern artist in the exhibition?

Azer Kerimov



Answer of yesterday's problem :

Alaaddin can take with certainty only 32 coins.

Note that Alaaddin can take 2 coins from each group of 3 unit squares of form L. Therefore, from each rectangle of size 2×3 he can get at least 4 coins. Since the 7×7 grid

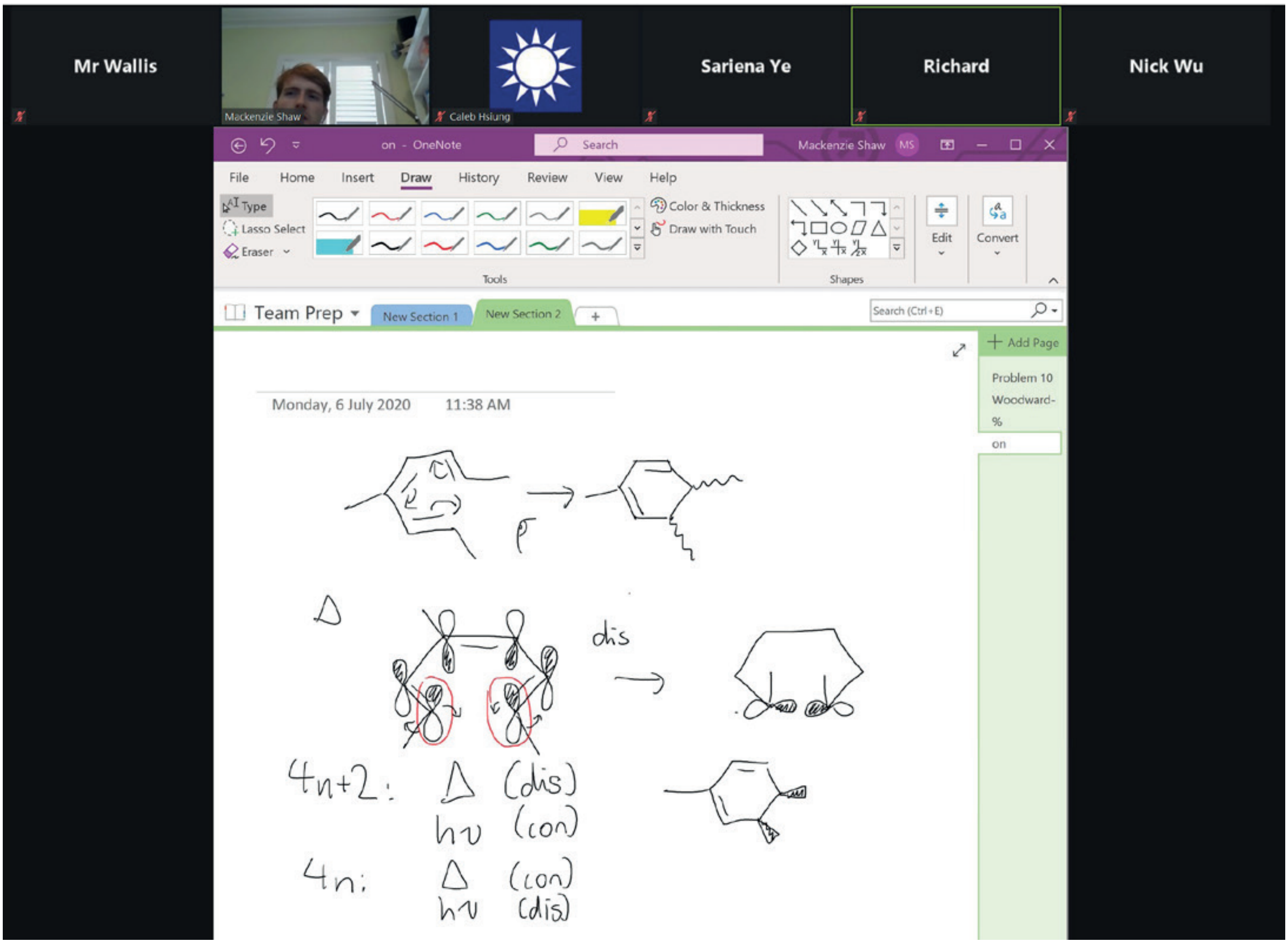
contains 8 such rectangles Alaaddin can take $8 \cdot 4 = 32$ with certainty (see the picture).

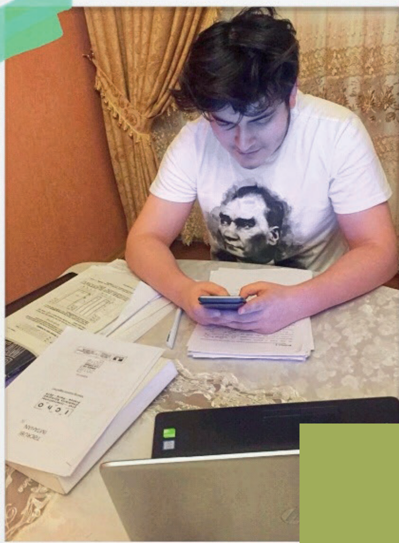
On the other hand, if the monster puts 16 gold coins into unit squares marked with a G and 33 silver coins into remaining unit squares then Alaaddin cannot take any gold coins. Therefore, he can take at most $49 - 16 = 33$ silver coins. Since Alaaddin takes an even number of coins the answer is at most 32.

NEWS FROM
NATIONAL TEAMS OF
COUNTRIES

AUSTRALIA

Final team training





AZERBAIJAN

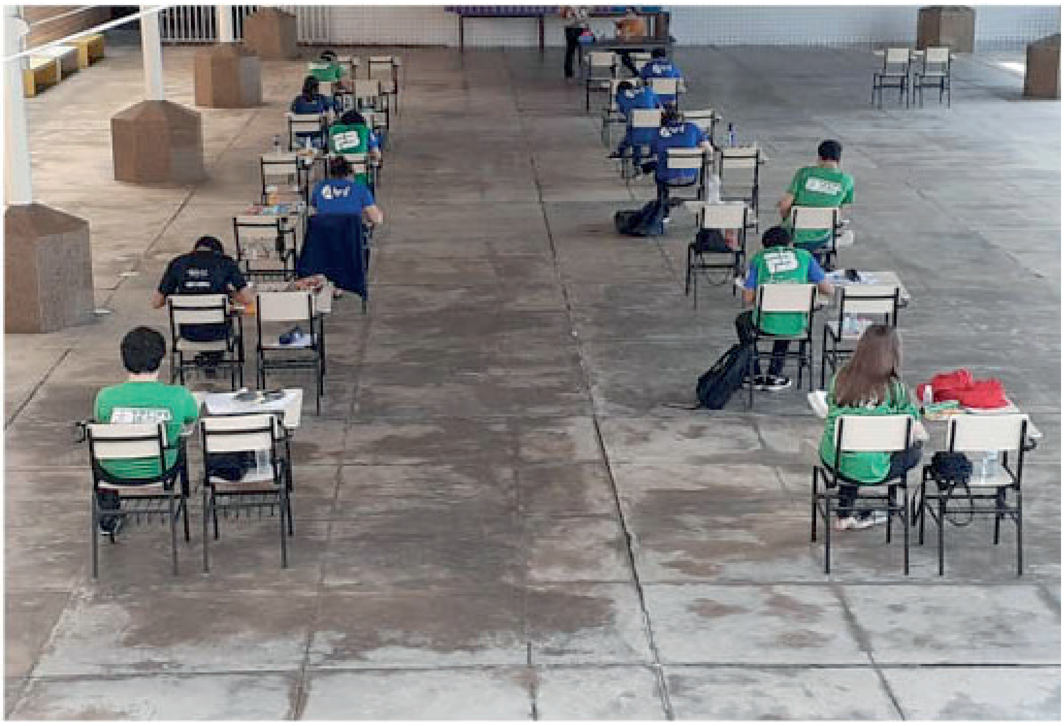
#StayHome #StaySafe and stay positive with high morale :)

BELGIUM

Regional selection round held in early March
before lockdown

BRAZIL

Brazilian Chemistry Olympiad, final exam.



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